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Microbial electrolysis cells for wastewater
treatment using inexpensive and sustainable
recycled carbon fibre anodes

Innovation Report

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Abstract

Vital to human survival and the protection of the environment, is the wastewater treatment industry. The practices employed work very effectively to protect human populations from pathogens and to safely treat water for discharge to the environment; securing future water supplies and protecting the rivers, lakes and seas. However, the drawback of this process is the high energy use, making the process expensive and a contributor to climate change. In the UK, approximately 3% of all energy is used by the water industry. The high energy costs also pose a problem for the developing world, as many nations cannot afford to treat their wastewater streams, resulting in unsafe discharge to the environment of raw untreated effluents.

The pollutants (organic and inorganic compounds) are a potential source of value and the industry is failing to recover the majority of this value. Some is recovered via the use of anaerobic digestors for sludge treatment and biogas production, but the majority of the recoverable energy is lost. A potential solution for this problem is the Microbial Electrolysis Cell (MEC), a subtype of a bio-electrochemical system.

The MEC is a system comprised of an anode, cathode and optionally; a membrane that separates the two electrodes. The MEC can sustain a biofilm on its anode which is electroactive and is able treat wastewater by facilitating the oxidation of the organic compounds, producing H_2 – a renewable and potentially sustainable energy source when produced by this method. The system requires the addition of a small voltage as the reaction is not spontaneous. However, this technology is not ready to solve the challenges the wastewater treatment industry faces, primarily due to its high capital costs but also its low energy efficiency recovery.

To address the capital costs, a recycled carbon fibre material (used for components in the automotive industry) was tested and shown to have electrocatalytic properties within an electrochemical cell, comparable to a commercially available graphite battery felt. The recycled materials were then used as anodes in 100 mL MECs using real wastewater, demonstrating potentially superior performance to graphite at a significantly reduced cost. This was confirmed at a larger scale (10 L) at a wastewater treatment plant, where hydrogen gas production and wastewater treatment performance were significantly superior but with a 96% reduction in the anode cost relative to the graphite felt used. A detailed cost benefit analysis using multiple TotEx scenarios confirmed the potential cost savings attributed to the use of the recycled carbon fibre anode, where an equally scaled MEC has the potential to be cost-competitive or less expensive than an activated sludge pool during a 20- or 50-year period. A placement abroad with a water technology consultancy did highlight that there are other technologies that are far more developed and are closer to commercial availability (i.e. sludge destruction via pyrolysis). The MEC offers something different and potentially, better, but larger scales are required to prove the technology.

The use of the recycled carbon fibre as the anode now makes larger-scale deployment of MECs far more likely. The significantly reduced capital cost but lack of performance compromise, mean that academia and industry alike can seriously consider the construction and testing of larger and more ambitiously scaled MECs. The material is a lower environmental impact (relative to virgin graphite and carbon), meaning that the life cycle impact of an MEC using the recycled carbon would be more less and more likely to have a positive impact, assuming performance optimisation. This could increase knowledge around the problems associated with upscaling and therefore, dramatically increase the likelihood of the technology becoming a commercially available product for water industries.

Acknowledgements

The number of people that I need to thank for having a contribution to my ability to submit this Innovation report are genuinely uncountable, so please, if you are reading this and feel you should have been included, don't take it personally!

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To the two people in my office who started this journey with me, Lavinia and Tina. We were the 'pioneers' of this CDT (at Warwick at least) and I feel that we have all grown up together because of it. Despite the fact that we've only known each other for four years, I feel we've been friends since I was a child. For me, both of you have had a massive impact – you have both inspired me to work harder than I ever have done, so I cannot thank you enough for that gift. It has been a pleasure to go on this journey with you! Sue, if you are also reading this, your constant support, encouragement and genuine excitement for myself, Lavinia and Tina has never failed to inspire me to keep pushing, so I feel like I can speak for the three of us when I say: thanks a million – you have been fantastic.

My family have been a constant source of support, even though our close nit group has been spread out over Europe (and even the world at one point). My sister, Jade (AKA “Fluffkins”), never fails to make me smile and laugh, which is the best gift anybody could ask for. My parents, Josh and Carla have always given me maximum encouragement and have always believed that I would be able to finish, even in the times when I felt it was impossible. I love you all so much.

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However, the biggest thank you has to go to my wonderful fiancé, Semina Ploumakis. Words cannot describe how much I have valued your support throughout this whole endeavour. You really inspire me, and it was during the most trying times that I would think of your work ethic, which would always push me to keep going. You have *literally* saved my life and I also cannot thank you enough for encouraging me to apply for this project back in 2015. *Ti amo amore mio!*

And finally, a few concluding remarks. This doctorate has been by far the hardest challenge I have (to this point at least) ever encountered. There were times when I literally wanted to (and literally did) cry out at the top of my lungs with joy and because of this project, and now, I live for those moments. The satisfaction of getting a result after years of work is brilliant and I really cannot recommend a doctorate enough (either PhD or EngD) to anybody who wants a fantastic challenge filled with joyous moments (ideally!). A major source of inspiration to want to succeed has been fuelled by my genuine (and sadly growing) concern for the environment. I hope that in some way, either this work

or whatever avenue I end up pursuing, results in positive to change to help protect the natural wonders of the world.

Thank you for reading and enjoy!

Daniel Indiana Carlotta-Jones

Author's Declaration

I declare that the work presented is my own and has not been submitted for any other award. All sources of published information have been acknowledged in the text by the use of references and bibliography.

Daniel Carlotta-Jones

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Definitions

AD – Anaerobic Digestion

ASP – Activated Sludge Pool

BES – Bioelectrochemical system

BOD – Biological Oxygen Demand

CapEx – Capital Expenditure

CHP – Combined Heat Power engine

COD – Chemical Oxygen Demand

MBR – Membrane Bioreactor

MEC – Microbial Electrolysis Cell

MFC – Microbial Fuel Cell

OpEx – Operational expenditure

SRB – Sulfate reducing bacteria

STW – Severn Trent Water

TotEx – Total Expenditure

WWTP – Wastewater Treatment Plant

Nomenclature

Bio-electrochemical systems – devices that are able to harness the ability of electrogenic microorganisms to exchange electrons with their environment to breakdown organic compounds to produce value. This could be in the form of energy or compounds of value.

Microbial electrolysis cells – subtype of Bio-electrochemical system that produce compounds (e.g. hydrogen, methane). Anaerobic/oxygen limiting and require additional voltage supply to function.

Microbial fuel cells – subtype of Bio-electrochemical system that produce electricity from the breakdown of organic matter. Aerobic and do not require additional voltage supply.

Electrogenic microorganisms/Electrogens – microorganisms that are able to freely exchange electrons with their environment. Example species is *Geobacter sulfurreducens*. They are considered to be the primary contributors to the operation of a microbial electrolysis or fuel cell.

Methanogens – microorganisms that produce methane as a product from the breakdown of organic compounds. They require anaerobic conditions to do this.

Sulphate reducing bacteria – microorganisms that use sulphate as a terminal electron acceptor when breaking down organic compounds. They are found in anoxic and anaerobic conditions and produce hydrogen sulphide, a toxic gas to humans as well as being a large cause of odours at sewage treatment works.

Wastewater treatment plant/Sewage treatment works – a site at which sewage is treated so that it is safe for discharge to the environment. This can include; chemical, physical and biological modes of treatment.

Preliminary treatment/screening – physical removal of large solids/debris which could damage assets further downstream or simply would not be

processable by the works (e.g. branches). The screening can be mechanical or passive.

Primary wastewater treatment – physical treatment phase at a sewage treatment plant. Typically for solids and BOD removal.

Secondary wastewater treatment – biological treatment phase at a sewage treatment plant. Typically for ammonia and BOD removal. Is followed by a secondary settlement stage for solids removal.

Tertiary wastewater treatment – final polishing phase of wastewater treatment. Typically for solids, phosphorus and ammonia removal.

Primary settlement tank – typical primary treatment asset at a sewage treatment works.

Activated Sludge Plant – large scale secondary wastewater treatment asset that uses aeration to enable aerobic microorganisms to conduct carbonaceous pollutant removal as well as nitrification of ammonia. They can have multiple lanes which are divided into pockets. Newer system.

Biofilter/Tricking filter – smaller scale secondary wastewater treatment asset that trickles primary effluent over a biofilm covered media (can be granite, plastic or blast slag) to treat wastewater. Older system.

Humus Tank/Final settlement tank – Secondary settlement stage for biofilters/ASPs. Removes solids. There can be returns from this asset back to an earlier stage of the works.

Tertiary Solids removal – polishing stage for removing solids prior to discharge. Can be a requirement for phosphorus removal if chemical dosing is used at the sewage treatment works.

Raw Sewage – sewage which has not undergone any form of treatment.

Crude sewage – sewage which has undergone screening at a sewage treatment works.

Primary Effluent/Settled Sewage – wastewater that has undergone primary treatment.

Secondary Effluent – wastewater that has undergone secondary treatment (including secondary settlement stage).

Final Effluent – effluent that has undergone all treatment stages at a sewage works and is discharged to the environment. Must adhere to the permit for the works that has been agreed with the Environmental Agency (in the UK).

Sustainable/sustainability – used to describe a process that when carried out, does not have a negative impact (be that economic, environmental or social).

Sewage sludge – sludges are concentrated solids that are by-products of primary, secondary and tertiary treatment processes at a sewage treatment works (and therefore, there are multiple subtypes). They must be treated prior to release to the environment as they can cause large amounts of environmental damage. There is the opportunity to recover value from sludge in the form of energy and fertilizer.

Anaerobic digester – a sludge treatment asset that processes sludge by using anaerobic microorganisms (namely methanogens) to convert organic compounds to methane and CO₂ (biogas). The biogas can be burnt to produce energy and heat. The solids remaining can be rich in nutrients and therefore, can be distributed to land as a soil treatment for agriculture.

1 Introduction

1.1 Severn Trent Water and the need for this project

Severn Trent Water (STW) is one of the largest water companies in the UK, second (in terms of customers) only to Thames Water, with almost 8 million people across the midlands.¹ They collect over 2.7 million m³ of wastewater per day all of which requires treatment before it is discharged back to the environment. Of all the UK water companies, STW are the only one to receive 4* ratings in 2 years out of the last three, achieving a 3* in 2019 (the ranking is between 1 and 4, where 4 is 'leading', 3 is 'good' and 1 is 'poor').² Therefore, they are arguably a high performer within the UK and have a strong desire to maintain the environment from which they abstract and discharge water.

For this reason, STW wanted to investigate potential alternatives to the existing wastewater treatment assets that are deployed to improve upon environmental sustainability. STW requires a technology that can treat water to the same standards which are already achievable from the existing wastewater treatment assets (and potentially better in the future) but with a lower environmental and economic cost.

This innovation report is the product of multiple sub-projects, including the following;

1. An overview and investigation into the need for wastewater treatment, how it operates and what its shortcomings are, to better understand what the potential solutions could be. Research of the potential solutions, with the identification of microbial electrolysis cells as a potential solution. A literature review of microbial electrolysis cells including their advantages, drawbacks and requirements for deployment for industrial wastewater treatment.
2. Literature and practical investigations to find ways of reducing the costs of microbial electrolysis cells (MECs) by identifying inexpensive anode materials and demonstrating their suitability as an anode for an electrochemical system.
3. Testing the developed materials in small lab-scale MEC systems using real wastewater
4. Proving MEC functionality at larger-scales with tests at a real wastewater treatment plant.

5. A cost-benefit analysis of the larger-scale systems, demonstrating the positive economic impact MECs can have if they are built economically.
6. A placement abroad with a water consultancy company to understand what they would define as innovative and to develop a clearer picture of what is required to deploy the MEC technology at larger-scales for the wastewater treatment industry.

An overview of how the submissions have led to the findings detailed in this innovation report are presented in Figure 1-1.

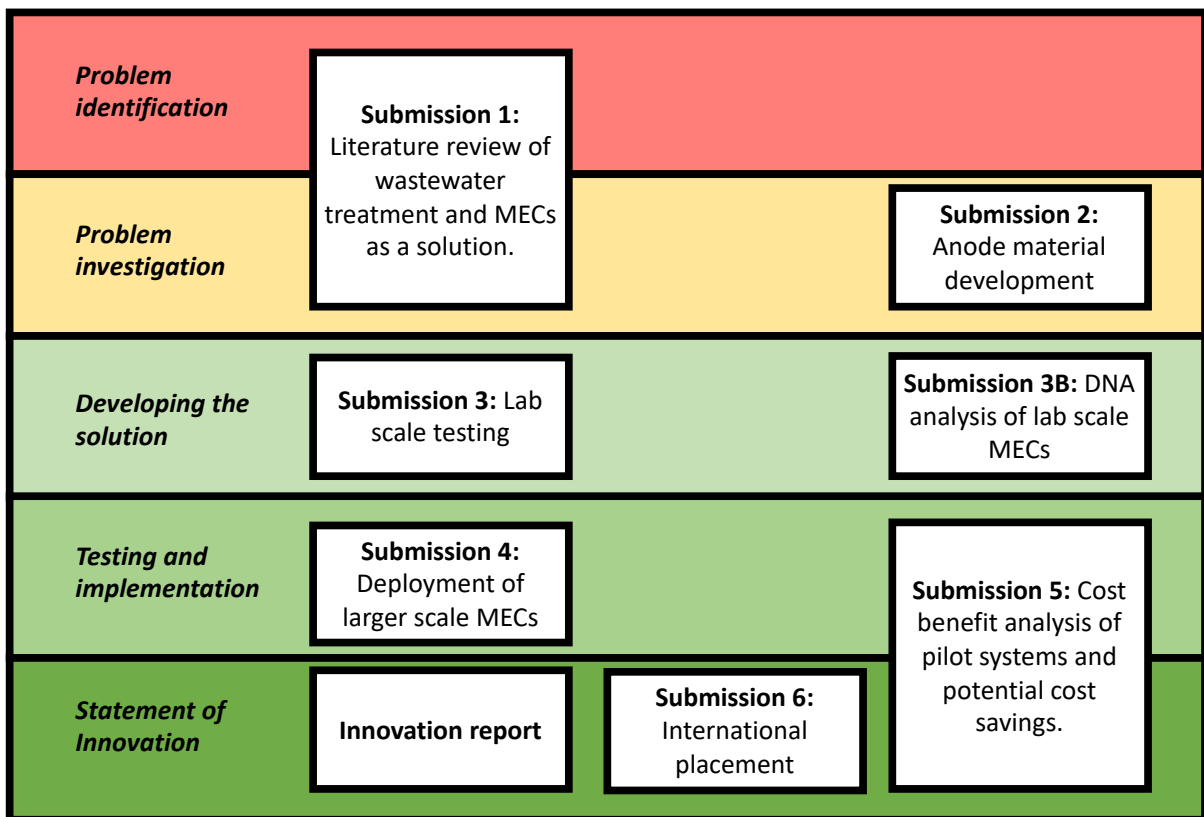


Figure 1-1: EngD portfolio overview, showing the stages to innovation and where the submissions and innovation report fit in.

1.2 The importance of sustainability and the threat of climate change

Achieving sustainable environmental practices is paramount to the survival of the human species and indeed, all other lifeforms on planet earth³. In time, ‘wartime’ like measures might be taken, where governments may have to exert control over its citizens in terms of their embodied carbon emissions from travel, food production/consumption and waste processing.

It is hoped however, that such severe interventions will not be required and that technological and behavioural strides to reverse the damages associated with climate change, will suffice. This must be achieved while preserving the relatively improved quality of life humans now experience (fewer famines, clean water access and longer life expectancies), tying in to the United Nations Sustainable Development Goals of ensuring access to modern energy services while increasing the share of renewable energy within the overall use.⁴ This ties into the economic and social sustainability that must be maintained by any innovations developed to combat climate change.⁵ This is for two main reasons:

1. Businesses will be unwilling to act on or make changes to their processes/products that will benefit the environment if the changes will be detrimental to their business. In this sense, the future of innovations that will contribute to improving the sustainability of the human race will depend on both economic and environmental benefits. A truly innovative product or process will not only preserve or improve on sustainability but will generate more value for the business by product creation or achieving cost-savings.
2. Socially, the livelihoods of individuals must be preserved. Any new idea or product that harms the job prospects for a particular industry, trade or specialism will not be popular, therefore, questioning the value of its innovation. This also ties into the economic factor, as job losses can end up harming the economic sustainability.

Therefore, any 'innovative' product designed to improve upon the sustainability of a process must not harm the social or economic sustainability of a business or country. An environmental solution that does not negatively impact social structures or economic sustainability could, therefore, be classed as innovative.⁶

1.3 The importance of wastewater treatment

Wastewater treatment (domestic and industrial) has been one of the greatest contributions to increasing the life expectancy of the human race and preserving the environment.⁷ Innovation within the field of wastewater treatment (in particular, over the last 100 years) has given humans the ability to remove dangerous pathogenic microorganisms which can cause disease in humans (e.g. cholera),⁸ as well as the

inactivation of organic and inorganic compounds⁹ which can lead to bacterial or algal blooms in water bodies,^{10,11} causing damage to the environment. As it is from the environment where water sources are abstracted (the term used for water acquisition from the environment),¹² there is a particular economic and social argument for its protection, with the added environmental benefit of maintaining high levels of biodiversity.

1.3.1 The wastewater treatment process

The basic premise of wastewater treatment is to move contaminated and potentially dangerous water after human use away from populations to a safe location for treatment.¹³ This is achieved via the use of the sewer system.

The treatment process occurs at relatively centralised wastewater treatment plants (this varies depending on the geography of an area). The process is multi-stage, where solids, physical debris, excrement, pathogens and nutrients are removed and inactivated. The main stages of wastewater treatment are described in Table 1-1.

Table 1-1: Processes and examples of different stages of the wastewater treatment process

Wastewater Treatment Process	Method of wastewater treatment	Example
<i>Screening</i>	Removes large debris from influent which could damage downstream processes. Debris includes dead animals, branches, wipes and non-biodegradable matter.	Fine screens. ¹³
<i>Primary</i>	Use of physical methods to remove solids. The solids removed here are usually in a “sludge” form and are processed in an anaerobic digester.	Primary sedimentation tanks. ¹³
<i>Secondary</i>	Use of biological methods to remove organic and inorganic pollutants. This can be the final stage of wastewater treatment if the quality of the effluent is high enough (i.e. BOD ⁵ lower than 25 mg L ⁻¹). ¹⁴	Activated sludge pools and Trickling filters.
<i>Tertiary</i>	Used as a final polishing step to remove pollutants and pathogens from wastewater. There can also be resource recovery from sludges produced during primary and secondary treatment (anaerobic digestion).	Anammox process, Tertiary solids removal. ¹⁵

The stages highlighted (Table 1-1) allow the treated water to be safely discharged to the environment, where the local water authority can reliably assume that there will be no adverse effects to the receiving waters. The water authority can determine whether the effluent could pose any risk to the receiving waters by measuring the

concentrations of organic and inorganic pollutants of both the effluent and receiving waters (some areas are more sensitive and require more stringent regulations).

1.4 The problems with wastewater treatment

Despite the efficacy of the wastewater treatment process to produce effluents that are safe for discharge, the assets used to treat wastewater are not flawless. The processes that are currently employed require improvement or in some cases, large overhauls if the wastewater treatment industry is become sustainable.

1.4.1 Financial cost

The operation of wastewater treatment assets requires large amounts of electrical energy. Over time, the quantity of energy required to run a wastewater treatment plant has increased due to the more stringent effluent demands imposed by governments and increased energy demands mean increased costs.¹⁶ This will (and is) being compounded by increasing energy unit costs (in terms of £ per kWh). It is estimated that WWTP in the EU expend anywhere between 0.3-2.1 kWh m⁻³ of treated wastewater.¹⁷

The primary areas of interest (where the bulk of treatment occurs) is during primary and secondary wastewater treatment. This is because they tend to be the most energy-intensive processes, with particular emphasis on the secondary wastewater treatment assets. The activated sludge plant (ASP) is an effective method of treating large quantities of wastewater to a high standard, but is a significant drain on resources for any wastewater treatment plant that employs them. The principal reason for this is the use of blowers in the ASP, which are required to aerate the sludge, enabling the aerobic microorganisms to metabolise the organic compounds and nutrients, thus treating the wastewater. Though effective, this process alone can account for over 60% of the total overheads for a wastewater treatment plant.¹⁸ By extrapolating the value of 0.3-2.1 kWh m⁻³, the energy consumption of the blowers could be up to 1.26 kWh m⁻³.

The ASP also has the drawback of a lack of direct value production from the treatment of the wastewater. The main by-product of the activated sludge process is waste activated sludge (WAS).¹³ WAS is difficult to dispose of and expensive to process

safely, as failure to do so can result in harm to the public from pathogens and damage to the environment.¹⁹ Unlike primary wastewater sludge produced from the physical wastewater treatment methods used in the primary phase of wastewater treatment, the sludge cannot be easily processed in an anaerobic digester due to the high water content.²⁰ The WAS can be dewatered and then processed in an anaerobic digester (AD), but this requires large amounts of pre-treatment, which involves high temperatures therefore greatly increasing the cost of WAS treatment by this method (also reducing overall sustainability of this process). In many cases across the globe, the WAS is buried in landfill, which is not only environmentally damaging, due to the release of green house gasses (GHG) such as methane, but is also failing to recover a large amount of value from the WAS, as it is rich in proteins and carbohydrates; a potential resource for the growing bio-economy.^{19,20}

1.4.2 Environmental costs

The majority of electrical energy produced and used in the UK has a carbon footprint associated with it. Ranked as the fourth largest consumer of energy in 2009, the wastewater treatment industry is a large contributor to the UK's carbon emissions.²¹ This is the equivalent to the electricity use of approximately 2 million UK homes (estimated using the calculation in. where the annual energy house of a home in the UK is 4,000 KWh - Equation 1-1).²²

$$\text{Equation 1-1: } \frac{100 \text{ GWh}}{4000 \text{ KWh}} = 2,025,000 \text{ homes}$$

As described in the previous paragraph, the quantity of energy is predicted to increase over time, due to a combination of increasingly stringent discharge limits (which are likely to require greater energy demands or processes to meet requirements) and increasing populations, resulting in the need for more wastewater treatment activity. This is also a clear indication of how the environmental and economic aspects of wastewater treatment are linked.

1.4.3 Wasted recovery

Anaerobic digestion does successfully recover some value from wastewater while simultaneously lowering the overall environmental footprint of the wastewater treatment processes. This is achieved via the production of methane from AD and its

subsequent combustion in a combined heat and power engine (CHP), producing electricity and potentially usable heat. This is immediately useful as the infrastructure to produce energy from methane is already available and well developed. However, AD cannot recover the majority of potential energy from the methane, as it's combustion in a CHP engine produces more heat than electricity (approximately a 65:35 split between heat and electricity respectively). In most cases, the location of the CHP engine on the wastewater treatment plant is too far from human populations to be of use to any local settlements. Of all of the available organics in wastewater, an estimated 28% is recovered as electrical energy via AD and CHP use, though this can be marginally improved with more efficient CHP engines.^{23,24}

1.4.4 Wastewater treatment infrastructure in less economically developed nations

It is estimated that 80% of the wastewater produced globally by humans is returned to the environment untreated.⁷ Approximately 11% of the World's population (780 million people) do not have access to treated water for domestic use and 35% of the World's population (2.5 billion people) lacked effective sanitation systems, or in other words, wastewater treatment infrastructure. A comparison of the quantity of wastewater treated by different countries with different wealth levels is provided in Table 1-2.²⁵ The UK falls into the high-income category (as do the majority of countries in Europe).

Table 1-2: Quantity of wastewater treatment by economic area

<i>Economic Standing</i>	Quantity of wastewater treated
<i>High Income</i>	70%
<i>Upper-middle Income</i>	38%
<i>Lower-middle Income</i>	28%
<i>Low-Income</i>	8%

As stated in section 1.4.1, there is a significant financial cost associated with wastewater treatment. There is not the ability to recover the majority of the associated costs (capital and operational), which will mean that less economically developed regions of the world cannot prioritise wastewater treatment, despite its vital importance.

To address this vital environmental conundrum, an innovative solution would be a less expensive wastewater treatment technology which is able to recover value, (and

ideally enough to make wastewater treatment a net producer of value before charging citizens/the state) meaning that poorer regions would be more likely to adopt wastewater treatment options. This would satisfy the three main criteria of sustainability: environmental, social and economic.

1.5 Innovation required to solve the problems associated with the wastewater treatment industry

It has been established that the wastewater treatment assets deployed today deliver high standards of wastewater treatment and environmental protection, but issues with cost (operational and capital), lack of value recovery and questions over the environmental sustainability are evident. Therefore, innovation within the industry would deliver; value recovery, lower operational costs (without compromising on performance) and smaller physical footprints.

1.5.1 Greater value recovery from wastewater

Despite the use of anaerobic digestion (AD) processes to recover energy in the form of methane, there are not many industrially applied systems that recover value from wastewater. There are investigations into nutrient recovery, such as ammonia and phosphate rich compounds,^{10,26} but more developments are required if the implementation of a circular economy for the wastewater treatment industry is to be achieved.

As the activated sludge process has the biggest shortcoming with regards to product recovery, any technology that can produce value from the wastewater that is usually destined for the activated sludge pool, could have substantial economic benefits for water companies. Depending on the product produced, chemicals of value could be sold on the market and if renewable energy is produced, the water company could offset the plant's energy demands by using any produced fuels/energy onsite.²⁷ Furthermore, the recovered product (regardless as to whether it is energy or a chemical of value) will have environmental benefits associated with their production, as energy/compound production from other sources would be reduced.

1.5.2 Less energy use than the activated sludge process

The greatest contributor to the operating expenditure (OPEX) of a wastewater treatment plant is the operation of the activated sludge pools (ASPs).^{18,20} A truly innovative wastewater treatment device would be disruptive by achieving a similar wastewater treatment performance as an ASP but at a significantly reduced energy demand. This could drastically reduce the operational costs of the wastewater treatment process as well as having a positive environmental impact. If less energy is used to achieve the same wastewater treatment standards achievable with an ASP, the carbon footprint of the whole process would be reduced.

1.5.3 Smaller physical footprint

Land use is slowly becoming more of an issue for wastewater treatment plants. The primary reason for centralising wastewater treatment is to take advantage of an economy of scale.²⁸ However, this means larger areas of land are required to process the wastewater of larger populations. The wastewater treatment plants all have a certain maximum capacity and are designed to be able to deal with population increases, but only to a point. The processes employed cannot be built “vertically” in the majority of cases (i.e. they cannot be stacked up on top of each other, which contributes to the large areas required to implement the technology). A stackable wastewater treatment device could address these issues, meaning more of the land at a wastewater treatment plant could be used for other processes, and any future wastewater treatment plants could be designed with less space in mind.

1.6 Existing technologies for recovering value and improving sustainability

There are several potential options for treating sewage and sewage sludge in a more economical and environmentally friendly way, which have different potentials and drawbacks.

1.6.1 Sustainable sewage sludge processing technologies

Sustainable sludge treatment options that have been well researched and developed include; pyrolysis and gasification, which are considered as 'sludge destruction' technologies.²⁹

Gasification uses very high temperatures and gasifying agents to produce gas for use as an energy source (hydrogen, syngas).³⁰ The process produces very little waste, but has the drawback of being very expensive to build and there are very few examples of larger-scale systems being used for wastewater sludge. Usually, they require the addition of a secondary product to function, meaning a secondary supply chain is required to maintain operation (e.g. wood chippings).³¹

Like gasification, pyrolysis also requires high temperatures with the additional requirement of an oxygen-free environment (e.g. argon or nitrogen only).²⁹ Pyrolysis can convert the sludge to products of value including; bio-oil, kerosene and syngas. The bulk of the solid product is in the form of bio-char. The biochar can be used as a soil remediator, slowing down the release of carbon to the atmosphere, theoretically enabling for effective carbon uptake by plant life. There are commercially available examples of this technology for sludge destruction, including: the PYREG unit (Germany) which specialises in the recovery of phosphorous for use in agriculture.³² There are still drawbacks, including the need for high levels of dewatering of the sludge (which like for AD, can be expensive) and the costs of operation are also high.

Both of these sludge destruction technologies, although potentially superior to anaerobic digestion, do not deal with the main problem highlighted previously, being the high costs associated with secondary wastewater treatment. Therefore, despite the potential improvements these technologies could deliver, they cannot significantly reduce the very high overhead costs or environmental impacts of the activated sludge plant on a wastewater treatment plant.

1.6.2 Example sustainable wastewater treatment technologies

Anaerobic up flow fluidized bed reactors (UASB) are a methane producing digester that is able to treat wastewater, forgoing the need for aerobic treatment and therefore; produces less sludge.³³ This has the benefit of the reduction in need of anaerobic

digestors or other sludge treatment processes. Furthermore, the biogas is produced directly from treatment and has a high methane content (hydrogen gas can also be produced).³⁴ The UASBs require higher temperatures than the ambient ones (during spring, autumn and winter) found in the UK and much of Europe, which is the main reason for their lack of use in those nations.³⁵

The membrane bioreactor (MBR) is such a technology that can treat wastewater to a very high standard, potentially higher than that of an activated sludge pool and with a smaller footprint. It also has the advantage of reducing the total quantity of secondary sludge, relative to an ASP. However, as MBRs are a newer technology, the capital and operational expenditure (from membrane replacement and energy use) is currently higher than that of ASPs and there are limited options to recover products of value (energy, chemicals, etc.), though there are examples where bio-ethanol production is possible.^{36,37}

Algae bioreactors are less developed than MBRs and UASBs, but have the potential to be deployed as a nature based solution to treat wastewater and deliver on the circular economy. Butanol and ethanol recovery is possible from algal treatment of wastewater.³⁸ Feedstock production and COD, nutrient and metal removal is also possible³⁹ and there is also the potential to recover phosphorus for use as a fertilizer.⁴⁰ Many of these treatment processes do require large amount of light and therefore, have high operational costs – this will be particularly costly in over the winter months (in the UK) when there is less daylight (not to mention the operational carbon emissions).

The bio-electrochemical system (BES) is also a potential option for wastewater treatment, which, appears to have the potential to combine the product recovery of sludge destruction technologies (AD, pyrolysis, gasification, etc.) with the capabilities of membrane bioreactors to treat wastewater with a smaller form factor (relative to activated sludge pools). After having investigated the problems with the wastewater treatment industry and the potential technologies that have been developed to address these concerns (with particular emphasis on improving sustainability), area with the greatest amount of potential was deemed to be the BES, which became the main focus of the EngD project.

1.7 Microbial electrolysis cells – the potential

Microbial electrolysis cells (MECs) are a subtype of bio-electrochemical systems (BES) and are a contender to be deployed as environmentally and economically sustainable wastewater treatment assets in the future. MECs treat wastewater using the naturally occurring microorganisms in wastewater and produce renewable energy in the form of hydrogen gas (or other products of value e.g. caustic soda,⁴¹ phosphorous,⁴² and ammonia).^{43,44} The other most notable BES is the microbial fuel cell (MFC), which does have similarities to MECs, in that it also treats wastewater but instead of generating a physical product, produces electrical energy directly. MECs were selected over MFCs due to the potential value of renewable and sustainable hydrogen.⁴⁵

1.7.1 How does an MEC work?

An MEC is a relatively complex system, as far as current wastewater treatment assets are concerned. Most MECs are made up of 5 main components: an anode, a cathode, a membrane, current collectors and a reactor chamber/vessel to hold it all together. A simple diagram of the components of an MEC are shown in Figure 1-2.

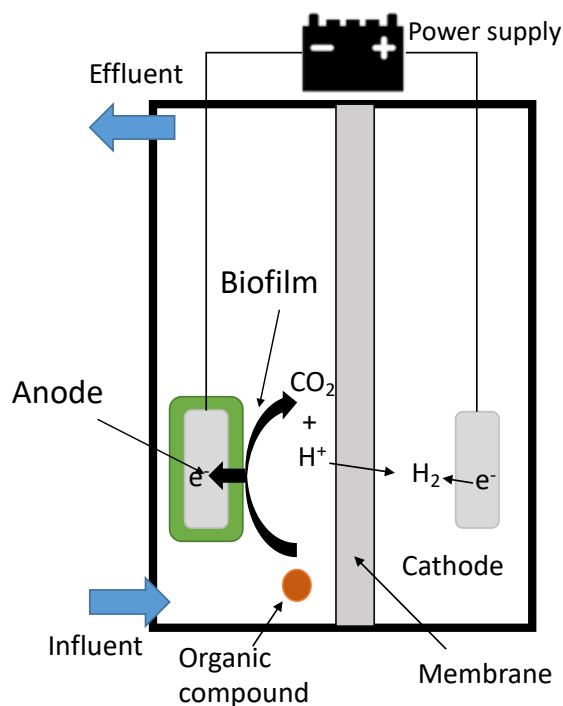


Figure 1-2: MEC structure and components

In MFCs and MECs it is the microbes that catalyse the anodic oxidation of organic compounds (it is at the anode, where microorganisms colonise, to form a biofilm, hence the term: “bioanode”). The microorganisms which colonise the anode can vary, with the drivers behind the action of BES being exoelectrogenic.⁴⁶ Exoelectrogenic microorganisms sequester electrons from a substrate and subsequently donate them to the anode on which they are growing, however when mixed consortiums of microorganisms are enriched using wastewater or wastewater sludge, non-exoelectrogenic microorganisms are also present.⁴⁶ In MFCs, the cathodic reaction (e.g. oxygen reduction, Equation 1-2) renders the complete BES reaction spontaneous, and power can be extracted. In MECs, additional power is applied to render the anodic, microbially catalysed oxidation reaction spontaneous with cathodic electrosynthesis (on the surface of the cathode), to produce hydrogen gas ⁴⁷ (Equation 1-3), caustic soda ⁴¹, methane ⁴⁸ or ammonia ⁴³.



This means that in the case of the MEC, an additional component to supply a voltage is required as there is no oxygen present (so the conditions are therefore anaerobic). At lab and pilot-scale, power supplies or a potentiostat are used to achieve this.⁴⁹

1.7.2 Materials

Within the literature, all of the materials used for the different components differ (in terms of make or subtype) but there are some general similarities. The anodes tend to be made of a carbon-based material, typically graphite or carbon felts, ^{44,50} which are traditionally used in battery systems.^{51,52} There are also examples of noncarbon-based anodes, where metallic materials have been used successfully.⁵³

The membranes can vary; both anionic and cationic can be used.⁵⁴ One of the more common membranes used in MECs are protonic exchange membranes (PEM), namely Nafion™.^{55,56} Separators can also be used which are not selective for any particular ion (e.g. Entek).⁵⁷ It is also possible to operate an MEC in the absence of a membrane.⁴⁴

As platinum is a known hydrogen evolution reaction catalyst,⁵⁸ its use as the cathode (or part of, via doping) as a standard material is prevalent in the literature,^{59,60} but is widely accepted as being unfeasible for larger-scales or real-world applications due to its cost. Alternatives are more widely accepted and researched now for all BES, due to the potential cost savings and comparable performances, including; stainless steel, nickel and activated carbon (examples presented in Table 1-3).^{55,61,62}

Table 1-3: Example cost of different cathode materials

Material	Price (£ Kg⁻¹)
Platinum	22,658.59 ⁶³
Stainless steel 316	2.27 ⁶⁴
Nickel	10.47 ⁶⁵
Activated carbon	0.86 ⁶⁶

The current collectors are how the anode and cathode are supplied with current from the power supply. These tend to be metallic (steel or titanium).^{67,68} The reactor vessels vary considerably in terms of materials, size, ratios⁶⁷ and architecture.⁶⁹

In lab-scale systems, the “H Cell” systems allow for an easy method of testing multiple variables,⁷⁰ however it is even possible to use small glass jars as the reactor chamber for an MEC.⁵⁹ The architecture can have a significant impact on performance, particularly in larger-scale systems.^{71–73} It is difficult to make direct performance comparisons between the architectures, as there are so many variables involved. However, the two more tested scaled-up designs tend to be: tubular^{74,75} and rectangular.^{67,76}

1.7.3 MEC Innovation type at present

There are currently no examples of MEC technology applied at an industrial scale. MECs are therefore not yet an innovative technology.^{77,78} However, if MECs are one day to be used for wastewater treatment applications and for the production of hydrogen gas, there is an argument that they would be a combination of disruptively and radically innovative. The radical ‘label’ stems from the fact that they would be a completely new method for treating wastewater where new and valuable products could be produced from wastewater at large scales, specifically within secondary wastewater treatment (when compared to biofilters and ASPs). The disruptive classification is due to the fact that the end goal of treating wastewater is a process

that is already used by society – this would just be another way of achieving it, but at lower running costs and with the added benefit of creating products of value at the secondary wastewater treatment stage (where currently, there is no product recovery due to the use of activated sludge pools and trickling filter systems).¹³

1.8 Problems with MECs that have halted their deployment

1.8.1 Capital costs

The ‘Achilles heel’ of the MEC is the capital expenditure (CAPEX) associated with their construction. Of the example pilot and lab-scale systems tested and investigated in the literature, the materials used made a scaled MEC too expensive to build when compared to an activated sludge pool (ASP). Despite the ability for an MEC to recover products of value, an assumed 20-year asset life (can be more) still makes the MEC significantly more expensive than an ASP, where both systems are designed for an equal population equivalent.⁷⁹ This is in spite of numerous improvements relating to cost reductions for the cathodes and membranes in particular. More significant changes will be required if MECs are to become an industrially viable technology for the wastewater treatment industry. Effectively, its payback period is far beyond the expected working life of the asset.

Aiken *et al.* conducted modelling on a pilot-scale reactor where it was determined (within certain organic loading rates and performances) a minimum cost reduction of 90% of the anode and current collectors was required.^{73,76} The high cost of the anode is attributed to the use of virgin graphite and carbon felts. These materials are very expensive due to the high energy usage required to produce the carbon felts and their subsequent graphitization (attributed to the need for temperatures up to 2200°C).^{80,81} It is now this combination of components, the anode in particular, which is halting the potential deployment of the MEC (assuming successful wastewater treatment capabilities and hydrogen gas production).

1.8.2 Inconsistent wastewater treatment capabilities

The second biggest issue that has been inferred from the literature, is the MECs capability to reduce the pollutant content of wastewaters to levels that are suitable for discharge. Thus far, there are no scaled examples of sufficient and importantly,

consistent, pollutant reduction for safe discharge to the environment (specifically concerning the organic content concentration). Table 1-4 details some of the results of average COD reductions of differing scales of MEC, from lab to pilot.

Table 1-4: Literature examples of pilot and lab-scale MEC COD reductions

Author reference	Scale of test	COD % removal	COD effluent concentration (mg L⁻¹)
<i>Cotterill et al. (2017)</i> ⁶⁷	Pilot-scale (100 L)	63.5	120.6 - average
<i>Heidrich et al. (2014)</i> ⁷⁶	Pilot-scale (100 L)	30-60	>125
<i>Escapa et al. (2015)</i> ⁷¹	Semi-pilot-scale (2 L)	10-70	>125*
<i>Escapa et al. (2012)</i> ⁸²	Lab-scale (200 mL)	44-67	121-238*

As the urban wastewater treatment directive (UWWTD) requires that effluents be returned to the environment with a maximum COD content of 125 mg L⁻¹,¹⁴ the four examples listed in Table 1-4 are not sufficient for continual safe wastewater treatment. It is possible that the nature of the MEC will never yield effluents that are safe for discharge to the environment alone and may require an additional ‘polishing’. This could be in the form of a tertiary treatment step, which is already standard in some wastewater treatment plants, or extra settling tanks (e.g. humus tanks for biofilters or final settlement tanks for ASPs).

1.8.3 Low product recovery relative to operational costs

Even though a scaled MEC could have approximately 10% of the running costs of an ASP,⁷⁹ an MEC should be recovering at least its own running costs in the form of hydrogen gas if energy neutrality is desired. The HRT for MECs appears to be critical in this regard, with higher HRT having better recovery than lower ones but with the downside of requiring more energy use per volume of wastewater treated. The *Beaza et al.* pilot had an HRT of 2 days (and periods of controlled medium feeds) and recovered over 121% of the input electrical energy.⁸³ *Heidrich et al.* reported an electrical energy recovery of close to 70%, short of the breakeven of 100% with an HRT of 1 day.⁷⁶ Lower HRTs (which are desirable to lower the footprint and therefore, capital costs of the system) tend to perform worse at larger-scale, where the Cotterill pilot had an HRT of 5 hours but an electrical energy recovery efficiency of 3.5% (although there will have been other mitigating circumstances that will have impacted the differences in performance).⁶⁷

1.9 Innovation required to successfully deploy MECs

Based on the problems discussed in 1.8, the main barrier that stops an MEC from being an innovative technology, are the high capital costs, which is primarily attributed to the cost of the anode. Although secondary, improvements to the wastewater treatment efficacy would also be desired, ideally to the point where no additional wastewater treatment steps are required. Failing this, the effluent produced from an MEC needs to be comparable to an activated sludge pool or trickling filter, so that any wastewater polishing treatment processes that are currently available would suffice. Finally, improvements to hydrogen gas recovery will also be desired to make the treatment of wastewater more environmentally and economically sustainable.

Therefore, the innovation required to successfully deploy MECs could be achieved by:

1. Using an anode material that is significantly less expensive than virgin graphite and carbon-based materials that have been used in previous MEC lab and pilot trials (at least 90% less expensive than the material used in previous pilot trials).^{73,76,79} The material should be able to successfully maintain an electrogenic biofilm and allow the MEC to operate, treating wastewater and producing hydrogen. The material must also be able to last for an extended period, ideally for 20 years, which is the standard lifetime of an asset used for wastewater treatment.
2. The anode material in question has to enable the MEC to perform as well as any virgin carbon-based materials tested. Ideally, they should perform better than any benchmark virgin graphite or carbon-based felt both in terms of wastewater treatment and hydrogen gas generation.
3. The replacement material should not have increased negative implications for the environment, especially when compared to virgin carbon or graphite felts. When building a system, the whole life cycle of the MEC should be considered. If the MEC in question is very unsustainable to produce, the environmental benefits of its operation may not be sufficient enough to justify its use.

The first output from the literature review of the wastewater treatment industry and MECs is that MECs must be cost-competitive (capital and operational) to deliver sustainable wastewater treatment. As it is the anode that is the most expensive

component of MECs, potential alternative materials were investigated and tested electrochemically to confirm whether there was the potential to use the materials as anodes for MECs.

1.10 Research aims for the project

The literature review generated a series of aims which had the potential to contribute to the development of MECs at a more fundamental level as well as at a larger scale at industry. These are presented in Table 1-5 and will be reviewed in the conclusions as to their contributions to science and the wastewater treatment industry.

Table 1-5: Research aims for the project

Chapter/submission number	Aim
2	Identify a suitable anode material that is inexpensive and is able to work as an anode in an electrochemical system.
3	Demonstrate that the inexpensive material is functional in an MEC (i.e. able to sustain a biofilm, treat wastewater and produce hydrogen gas)
4	Upscale the MEC, demonstrating that the materials can work in architectures which are more representative of a real world example.
5	Cost benefit analysis of the upscaled MECs where the potential cost savings of the MEC can aid in deployment and make the MEC cost competitive with existing wastewater treatment assets.

2 Identifying a new anode material for MECs

2.1 What does an innovative MEC anode material need to do?

Any anode material used in an MEC must be:

1. Conductive: the conductivity of the material will aid in the performance of all BES (including MECs).⁸⁴ If the anode material is more conductive, electrogenic microorganisms will be able to donate their sequestered electrons from any organic compounds more readily, to the surface of the anode material.
2. Able to support the growth and maintenance of an electrogenic biofilm - as it is the surface of the anode on which the microorganisms must grow, the materials must be able to readily sustain and maintain a biofilm.
3. Withstand the conditions of wastewater (and liquid in general). The material is going to be permanently submerged in wastewater and therefore, the anode has to be stable and resistant to the changeable conditions of wastewater (i.e. temperature, pH and solids that could cause damage). It must also be resistant to the microbial activity (e.g. it can't be used as a food or damaged by any of the microbial processes).
4. Achieve the previous three points at a suitably low cost: there are numerous battery electrode materials that have been tested in MECs and work, but their cost is too high for a large-scale application. Only with a large reduction in cost tied in with the potential high performances of graphite/carbon felts with MECs be able to deliver on their potential as sustainable wastewater treatment units.

2.2 Potential candidates for replacement of graphite and carbon felt

Examples of various anodes that were functional in MECs were collated and compared from a cost perspective. Two examples used in pilot-scale systems are listed in Table 2-1.

Table 2-1: Anode material costs in known examples of BES (MECs and MFCs)

Reference	Anode material	Material type	Price (£ m⁻²)
<i>Cotterill</i> ⁶⁷	SGL GFD 4.6	Graphite	88-218
<i>Heidrich</i> ⁷⁶	Olmec	Carbon felt	285.9

The costs of these materials are all too high for large scale use at a wastewater treatment plant, despite their relative efficacy in terms of hydrogen production and wastewater treatment (in particular the Olmec felt used in the *Heidrich* pilot)^{73,76}. Significantly less expensive materials are desired, so an investigation into potential unknown electrode materials was conducted to identify potential options for larger-scale deployments. The graphite felt used in the *Cotterill* pilot was used as a form of control, as it is significantly cheaper than the Olmec mat listed in Table 2-1 and it worked in a pilot-scale example (total volume of over 100 L).⁶⁷

2.2.1 Woven carbon fibre grids

Carbon fibre twill (MB Fibreglass, 200 g m⁻²) is a highly woven material. Carbon fibre woven materials have been used in MECs as anodes so this suggested that this material would work as an anode.⁸⁵ The material cost £20 m⁻² (£100 kg⁻¹) is significantly less expensive (between 4 to 14 times) than the graphite felt baseline and the carbon felt example listed in Table 2-1. The twill also had the advantage of being very flexible, so it could be suitable for a multitude of different architectures and configurations, which was one of the principal reasons for its selection. As the carbon fibre twill was also already produced as a flat sheet, it was assumed that no additional major alterations would be required for its use as an anode in an MEC. There are examples of some major manipulations required for carbon fibre anodes, including weaving and sewing of the fibres to produce usable MEC (or MFC) anodes.⁸³

2.2.2 Recycled carbon fibre

During most processes, waste is an undesired by-product. Efforts are always made to reduce the quantity produced, but a portion will always end up being unusable for its original purpose (be it food-related,⁸⁶ textiles⁸⁷ or metal processing). The processing, cutting and sizing of carbon fibres for use in the automotive and aerospace industries is no different.⁸⁸ ELG Carbon Fibre Ltd. states that approximately one third of all carbon fibre processed will end up as waste.⁸⁹ The Green Alliance report that carbon fibre waste will pose significant environmental problems in the future,⁹⁰ so efforts to create a more circular economy early on should be employed (it is easier to deploy a circular economy to a new product or industry than an older one). The quantity of waste produced is made more scandalous by the fact that carbon fibre production is

very energy intensive (approximately 200 MJ/Kg or 55 kwh/Kg - as discussed in section 1.8.1).⁹¹ Recycling the carbon fibre is postulated to be in the region of 2 MJ/Kg, significantly lower than the virgin fibres. Therefore, if carbon fibre waste is an unavoidable by-product, an application for it must be found, to recover the value from the wastewater material, but also to stop it from reaching landfill or the environment, where it can cause damage.

There are examples of non-woven carbon-based felts being used as electrodes in MECs.⁹² As Carbiso-M is a non-woven carbon mat it was postulated that this material could be used as an anode for MECs and potentially, other electrochemical systems (batteries, fuel cells, etc.).

The reason for its use was not purely for the potential environmental savings, but also for the greatly reduced costs compared to other battery felts that have been used in MECs in the literature. The Carbiso-M costs as little as £18.42 kg⁻¹ but the price per unit of area is dependent on the thickness required. A breakdown as to what that would cost for different thickness mats is defined in Table 2-2.

Table 2-2: ELG Carbiso-M price comparisons for different GSMs

Mass per unit area (g m ⁻²)	Price (£ m ⁻²)
100	1.84
300	5.52
500	9.21

Any MEC used at an industrial scale for treating wastewater will need large amounts of anode which means that the high prices of virgin graphite and carbon felts would make the capital costs very high (and in the majority of cases, too high to be economically viable). Using the Carbiso-M might be a method of drastically reducing the costs of the MEC, potentially to the point that allows for deployment. The savings compared to graphite felts could be in the order of over £200 m⁻² of anode, and therefore, easily over the 90% saving requirement for the anode.⁷⁹

2.2.3 Manganese (IV) oxide coatings

There are some examples of BES where metal catalysts on an electrode can aid in boosting the performance of the systems, which may be required if the costs of their running are to be recovered. Ruthenium has been demonstrated to boost performance

but is too expensive to be used at larger-scales⁹³. A less expensive and potentially, innovative method of improving the performance of an MEC could be the use of manganese (IV) oxide coating of the anodes. MFCs using carbon paper anodes coated in manganese (IV) oxide have demonstrated increased performance.⁹⁴ The electrodeposition of the metal oxide uses manganese (IV) acetate as an electrolyte, which is an easily manufacturable and relatively low-cost chemical (\$1 kg⁻¹ if purchased from Asia in bulk).⁹⁵ Little research has been conducted to develop this further and it is postulated that this is due to the lack of an extreme gain in performance observed, relative to the overall cost of the anode. In essence, if the anode material is already too expensive to use at large scale, the marginal boost in performance with the increased expense of the coating materials and process, will not be the key to unlock this technology, and is, therefore, not innovative or applicable at larger-scales. However, if instead a far less expensive base material is used, the performance boost may be worth-while. Therefore, the attempt to electro-coat the recycled carbon fibre anodes with manganese oxide could well be the innovative approach to deploying the technology.

This then produces the following questions:

1. Can recycled carbon fibre mats used for structural components (which is far less expensive and less environmentally taxing compared to virgin carbon and graphite materials) work as electrode materials?
2. Can they conduct electricity and facilitate electrochemical reactions like other industrially tried and tested anode materials?

A further point is that the ELG materials are derived from waste and currently, do not have many large-scale applications in industry, so finding a use for them will provide value and encourage the recycling of waste carbon fibre, promoting a more circular economy.

2.3 Experimental procedures – assessing the material

Details of the experimental procedures used to test the electrochemical activity of the recycled carbon fibre materials, by setting up electrochemical cell systems are given in brief in this innovation report. The purpose of these experiments was to establish

whether these materials could serve as suitable replacements for virgin battery graphite and carbon-based felts in microbial electrolysis cells.

2.3.1 Materials

The reactor chambers were manufactured out of polycarbonate blocks which were machined using a CNC (computer numerical control) machine, with an internal volume of 50 mL for each electrode chamber (an overall cell volume of 100 mL). The final assembled cells are shown in Figure 2-1.

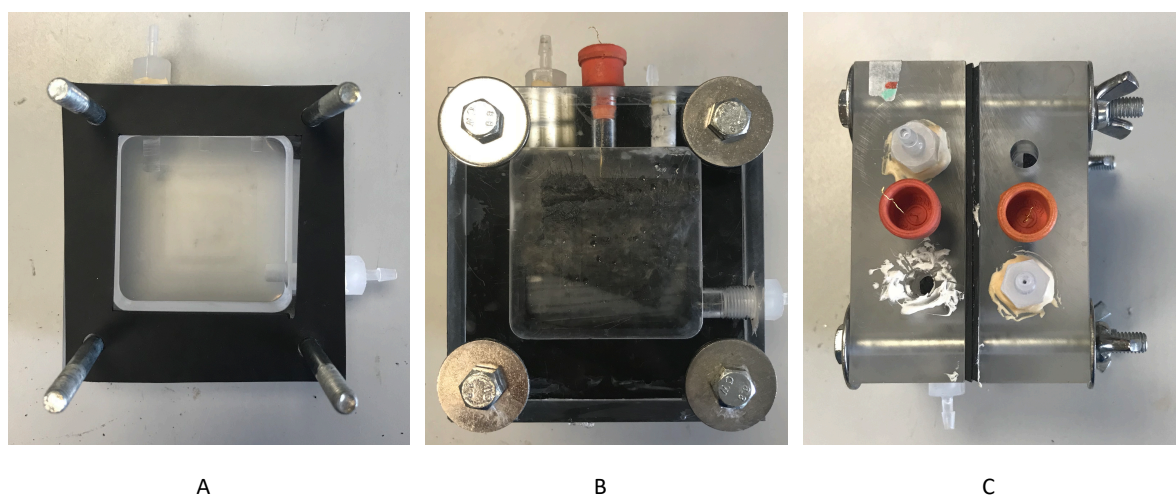


Figure 2-1: Electrochemical Cell construction. Images show different angles and stages of assembly.

A) Internal compartment of the cell. B) Side view when cell is bolted together. C) Top view of cell when fully assembled, showing connections for working and counter electrodes (wires guided through red stoppers). Open holes for reference electrodes are shown. Input and output hose points were not used for this experiment.

Reference electrodes

Reference electrodes were handmade, using glass tubing (5 mm internal diameter, 7 mm external diameter), a molecular sieve bead (~5mm) and silver wire (0.5 mm 99.9%, Alfa Aesar) coated in silver chloride by dipping the wire in 10 % sodium hypochlorite for 10 minutes and subsequently washing with RO water for 20 minutes. The wire was then air-dried. These components were assembled and the electrode was filled with 3M KCl solution. When fabricated, all electrodes were tested against each other to determine that they had the same potential against a commercial Ag/AgCl reference electrode (Sigma Aldrich), as well as each other (± 5 mV).

Carbon-based anode materials

Electrodes were constructed from graphite felt of thickness 4.6 mm (GFD 4.6, SGL Group, Germany) and two different thicknesses of recycled carbon fibre mats (M Carbiso M100 and M300, ELG, UK) and a carbon twill (200 g m⁻², MB Fibreglass, UK). The area of the electrodes was 4.5 cm² and was cut using an engineer's square and a scalpel. The SGL GFD 4.6 mm felt served as the benchmark for the experiments.

Electrodeposition of manganese (IV) oxide coatings

The manganese (IV) oxide coatings were deposited using a Gamry 600+ potentiostat with a Gamry ECM8 multiplexor. This method was adapted from Zhang *et al.*⁹⁴

Before electrodeposition, anode materials were cleaned first with 10 % (v/v) hydrogen peroxide and then with 10 % (w/v) hydrochloric acid, both at 90 °C for three and one hours respectively. A 0.25 M solution of manganese acetate was used as the electrolyte for the electrodeposition for 1 hour for each electrode. A 0.8 mm 316 stainless steel wire was used as the current collector to connect the anodes to the potentiostat clips. The electrodes were weighed before and after to ensure that there was consistent electrodeposition of the manganese (IV) oxide.

2.3.2 Electroactivity assessment of anode materials by cyclic voltammetry

To observe the impact on electron transfer, cyclic voltammetry (CV) scans were performed on the carbon-based anodes. The scans were conducted between -400 and +700 mV vs. Ag/AgCl. The measurement of the currents is a determination of the electron transfer rate from an analyte to the working electrodes⁹⁶, which indicate the conductivity or potential usefulness of a material in an electrochemical system; required to identify the potential innovation of the use of recycled carbon fibre in an electrochemical system. The CV scans were conducted with the M9 media with and without hexacyanoferrate (added to the media in both chambers) to a total concentration of 10 mM.

Counter electrodes were made from the M100 material at three times surface area of the working electrodes, to ensure a sufficient rate of reaction at the counter electrodes at benign voltages between the working and counter electrodes.⁹⁷

2.3.3 Morphological characterisation of carbon-based anode materials by SEM

SEM (scanning electron microscopy) imaging was used to assess the morphology of the different anode materials which were fabricated. This was to determine if there was an observable coating of manganese (IV) oxide applied to the fibre.

2.4 Results: a potential candidate for a replacement to virgin carbon-based anodes for BESs emerges

2.4.1 Carbon fibre twill failure

When cut, the carbon fibre twill (MB Fibreglass, 200 g m⁻²) began to flay rapidly and was very prone to falling apart. To combat this an epoxy resin (Scotch-Weld DP 760, RS components) was used, which gave the weave structural integrity, reducing the flaying and eventual unravelling of the carbon fibre twill. However, they were very brittle when set and were prone to breaking when placed inside the MEC chambers (Figure 2-2).



Figure 2-2: Carbon fibre twill with Scotch-Weld DP 760 fractured epoxy frames.

The Scotch-Weld DP 760 epoxy appeared to fall apart during the electrodeposition of manganese (IV) oxide on the carbon fibre, so an alternative epoxy, Super-Sap, was then tested as a replacement. The Super-Sap was incompatible with the carbon fibre twill, as it was too viscous and spread all over the very flat surface of the twill, drying over the whole area, meaning electrodeposition of the manganese (IV) oxide was not possible and there was not a method to stop the flaying and degradation of the twill during manipulation or anode preparation. A physical clamp mechanism would likely be required to reduce the flaying of the twill, but as the twill was very prone to damage and mass loss, the material was deemed unsuitable for this application.

As the recycled carbon fibre mat did not have the same problems as the twill, it was decided to proceed with the electrochemical tests with only the recycled carbon fibre materials and the graphite felt (both with and without manganese (IV) oxide).

2.4.2 Electroactivity assessment of anode materials by cyclic voltammetry

All of the plain carbon-based anodes (recycled carbon fibre and graphite felt) produced very small currents during the potential sweeps of the cyclic voltammetry tests (Figure 2-3: black traces, scans A-C). This demonstrated that the experiment was within the solvent window (that solvents in the electrolytes were stable within the oxidation and reduction potential range of the experiment).⁹⁶

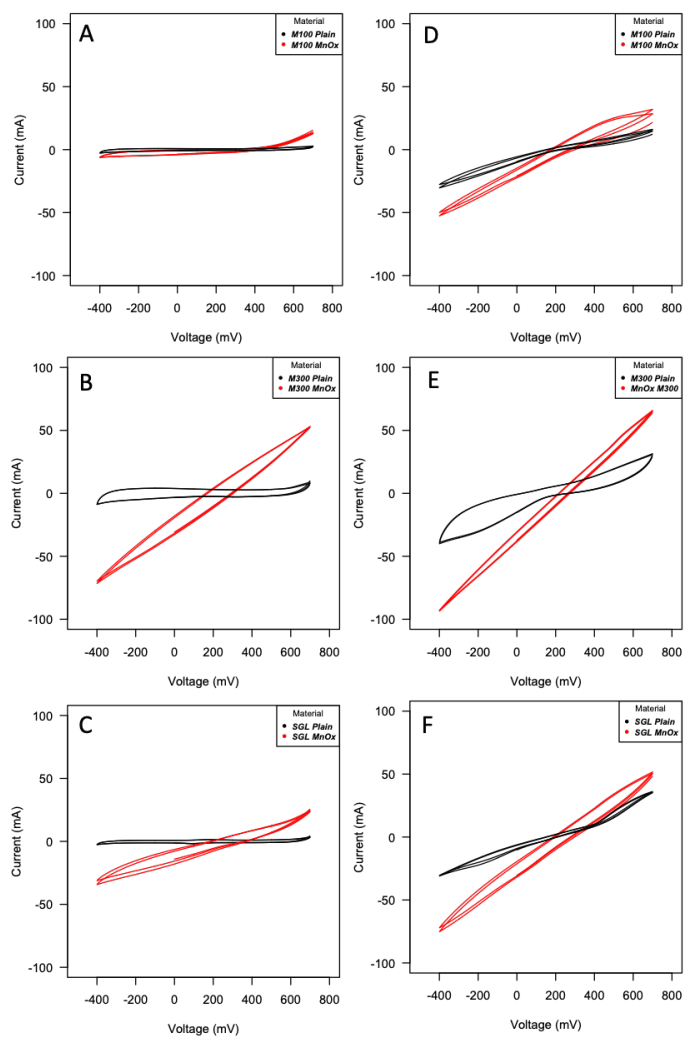


Figure 2-3: CV scan comparisons

(A-C) were recorded in M9 microbiological media. CVs (D-F) were recorded in M9 microbiological media with the addition of 10 mM potassium hexacyanoferrate. All CVs compared an uncoated material to its coated variant.

Small differences in capacitive currents were visible, where M300 showed larger hysteresis in the oxidative and reductive sweeps (Comparing M300 (B) to M100 (A) and SGL GFD (C)). Electrodeposition of MnOx on M100 increased the currents slightly (A), whereas the coatings on the M300 and SGL GFD yielded considerable current increases with steeper CV curves (B-C, red curves in all cases), with a zero-current transition around +200 mV vs. Ag/AgCl. The addition of hexacyanoferrate led to higher currents in all cases (D-F), while with the plain electrodes (black traces) a plateau-like transition near +200 mV vs Ag/AgCl was seen, steeper CVs were observed upon MnOx coating (red traces).

Water oxidation and proton reduction would be negligible within the window selected (-400 to +700 mV Ag/AgCl) ensuring the conditions of the experiment were within the solvent window. The +200 mV vs. Ag/AgCl midpoint (Figure 2-3 – all scans, red traces) of the transition between negative and positive current correlates closely with the standard reduction potential (at pH = 7) of $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ (206 mV vs. Ag/AgCl)⁹⁸ as well as $\text{MnO}_2/\text{Mn}^{2+}$ (172 mV vs. Ag/AgCl)⁹⁹. Both the MnOx coating, and the hexacyanoferrate supplementation gave rise to higher currents and thus, served as redox agents under the CV conditions used.

The redox activity of the MnOx coating is reminiscent of the function of manganese oxides as anodic material in alkaline batteries¹⁰⁰. Though it is the aim of this project to use these materials in an MEC, a potential offshoot of this finding is that the recycled carbon fibre electrodes that are coated with the manganese (IV) oxide could be used as electrodes in manganese oxide batteries, helping to make them less expensive to manufacture and with less environmental implications, due to the use of the waste material over a virgin one. Therefore, this could challenge the current method of manufacturing manganese oxide batteries, making it a potentially disruptive innovation for that industry (but this would require further testing to confirm). As the aim was to create a material for MEC technology, the materials use in another industry would be an architectural form of innovation.

Quantitative comparisons of the different materials (in terms of the electrochemical activity; the current at +700 mV vs. Ag/AgCl) was identified and is listed in Table 2-3.

Table 2-3: Current generated in cyclic voltammetry with different anode materials, normalised to equal front surface area.

Material type	Area density (g m ⁻²)	Normalized currents (A m ⁻²)			
		M9 electrolyte		M9 electrolyte + 10 mM potassium hexacyanoferrate	
		No coating	MnOx coated	No coating	MnOx coated
SGL 4.6	465	1.56	12.27	16.82	24.82
Carbiso M100	100	0.90	7.58	7.14	14.40
Carbiso M300	300	3.97	22.51	15.49	28.20

If a current generation from a particular material is similar to that of the graphite felt (SGL GFD 4.6), there is an argument that the material will also work as an electroactive surface for which to cultivate biofilms in an MEC. In the M9 media, manganese oxide coatings enhanced the current at +700 mV vs. Ag/AgCl by 7.9x (SGL), 8.4x (M100) and 5.7x (M300) with respect to the plain materials. The addition of hexacyanoferrate increased the current by 10.8x, 8.0x, 4.0x, respectively, while the currents produced by the materials with both the manganese oxide deposition and hexacyanoferrate addition were increased by 15.9x, 16.0x and 7.1x. The currents were highest for the manganese oxide coated electrodes in hexacyanoferrate-supplemented electrolyte, for all electrode materials. The currents generated at +700 mV demonstrate the ability of the recycled materials to generate currents and, potentially, act as an alternative to the graphite felt in an electrochemical system, both with and without the manganese (IV) oxide.

In all cases (except for the plain electrode in hexacyanoferrate solution) the M300 exhibited the highest normalised current, followed by the SGL benchmark and finally, the M100. A large difference in current generation between the M300 and M100 was expected, when taking into account the differences in area density when electrodes of the same front surface area are used. The SGL material, however, has the highest area density and thus was less effective in the reactions tested compared to the M300 mat. This was particularly notable for the currents generated from the electrolytes that were hexacyanoferrate-free and using manganese (IV) oxide coatings as electron acceptors (Figure 2-3 a-c and Table 2-3), a situation similar to alkaline battery anodes.

In this instance as well, the M300 materials were able to generate higher currents than the SGL graphite felt. As the recycled carbon fibre materials are far less expensive, when compared to the graphite felts, this could be beginnings of a far less expensive electrode material for MECs which could allow for their deployment at large scales.

2.4.3 Morphological assessment of carbon-based anode materials by SEM

The MnOx coated fibres (Figure 2-4 B) were thicker when compared to the uncoated (A) material, appearing brighter in SEM due to the manganese deposition when compared to areas where the coatings had been removed (Figure 2-4). The manganese (IV) oxide increased the thickness of the ELG M Carbiso fibres by ~55%, as particularly evident from Figure 2-4 B. From a qualitative perspective, the electrodeposition of the manganese (IV) oxide appeared even across the fibres.

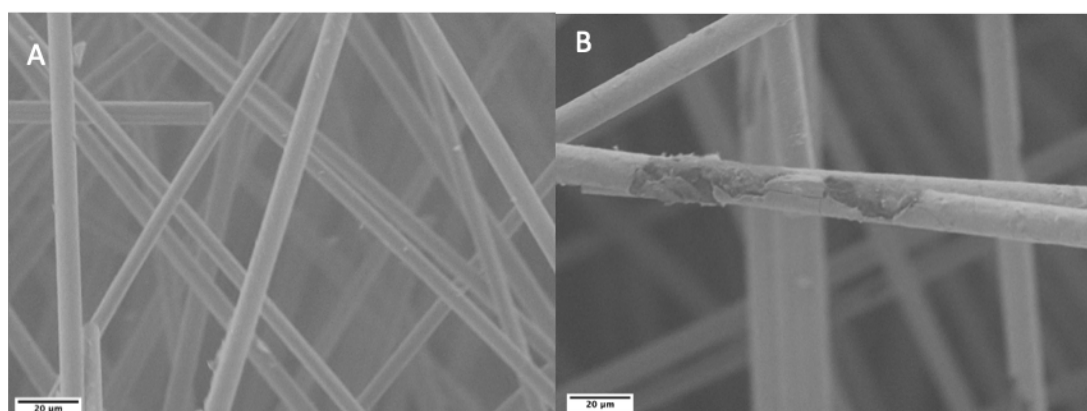


Figure 2-4: SEM images of Carbiso M fibres -at 1000x magnification

SEM micrographs of the SGL GFD 4.6 felts are shown in Figure 2-5. As with the ELG fibres, the SGL felts were also composed of fibres that were visualised easily at 1000x magnification (Figure 2-5 A) and appear similar, differing only in that the SGL graphite fibres were ~33% thicker in diameter compared to the ELG fibres. The manganese (IV) oxide coating process was equally successful in terms of homogenous and even coating (Figure 2-5 B).

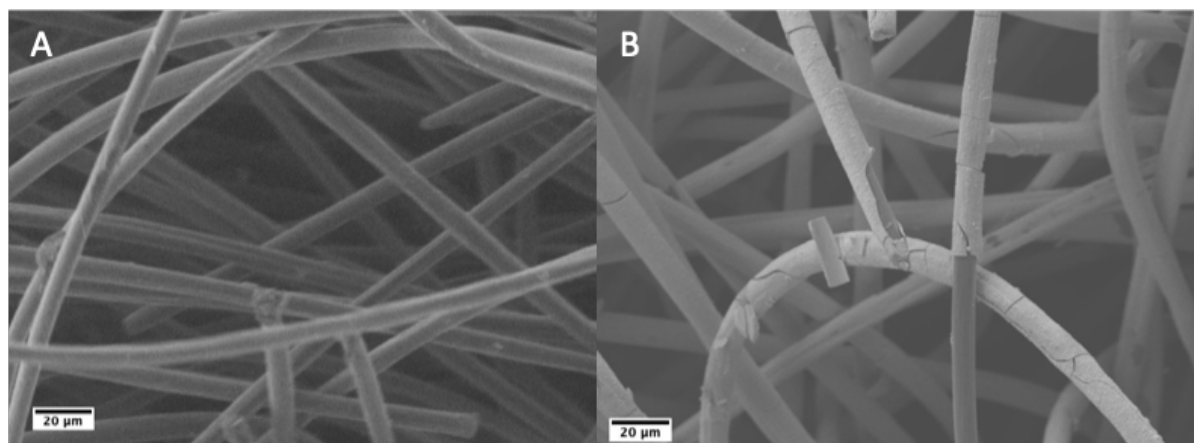


Figure 2-5: SEM images of SGL graphite fibres at 1000x magnification

2.5 Potential innovation

Carbon-based felts (including graphitised ones) are among the most widely used materials in battery systems. There is also a growing interest in the use of carbon fibres as anode materials in electrochemical systems in general.^{101,102} The use of the recycled carbon fibre mats (Carbiso-M: M100 and M300) is a novel concept – recycled carbon fibre is not a widely used commodity in its intended industry (structural components in the automotive sector) and thus far, there have been no recorded examples to date of its use as an electrode material in a battery, fuel cell or any bioelectrochemical system. It has been confirmed that these recycled materials are conductive and can facilitate redox activity, which may also be observed in microbial electrolysis cells – but novelty and innovation are not the same thing.⁷⁷ For this novel idea to be disruptively and radically innovative, it would have to be applied at an industrial scale in MEC technology and challenge the status quo of wastewater treatment assets (or some other electrochemical systems). At this stage, there are two major benefits the ELG Carbiso-M has over virgin graphite and carbon felts which may allow for the deployment of larger-scale MECs; an environmental and price saving.

2.5.1 Environmental benefit

The use of a recycled carbon fibre electrode would have positive environmental impacts over virgin carbon or graphite felts. The majority of the material that is used to manufacture the carbon fibre mats would, under normal circumstances, be disposed in landfill. Therefore, the generation of a new market for the use of recycled carbon fibre (i.e. MEC, fuel cell or battery anodes) will stimulate the overall use the waste carbon fibre in a greater number of industries that required battery technology, which will further incentivise the reuse of any waste produced by the manipulation of virgin carbon products. An LCA conducted into the use of the recycled carbon fibres over virgin carbon fibre in the automotive industry indicated that there were significant environmental benefits to the use of the recycled fibres,¹⁰³ a benefit that would also be replicated if they were used in electrochemical systems (including MECs). There it the potential to reduce the energy cost of carbon felts used in MECs over over 100 fold (200 MJ/kg down to 2 MJ/kg).⁹¹ It is important to consider the environmental impact of constructing new assets when considering the concept of “whole system design”, especially if the technology is being designed to improve upon sustainability.¹⁰⁴

2.5.2 Cost-saving

The ELG recycled carbon fibre mats (M-Carbiso) are significantly less expensive than any virgin graphite or carbon felts that are currently on the market. Though there is an argument that carbon-based materials do not have to be used for the anode,⁵³ there is already a large supply and demand for their production, use and trading on the market. They are also easy to manipulate to use in systems such as MECs – the dimensions, sizes and stability in water (specifically wastewater) are now proven.

The recycled carbon fibre is inexpensive to purchase - M100 and M300 cost £2.18 and £6.54 m⁻² (the price per m² when ordering a single roll of the fibres – larger orders would reduce these prices). At £87 m⁻² (assuming purchase orders of 100 m² or more), SGL GFD 4.6 is simply not competitive from a capital cost perspective. If successfully deployed in battery or other electrochemical systems (namely MECs), the capital costs of future devices could be significantly reduced (between 92-97% saving).

The fact that these mats are conductive, are stable in liquid and crucially, are inexpensive (especially when compared to virgin carbon material alternatives) bodes well for their use within MEC technology. Before doing a more detailed cost benefit analysis, the potential of the materials to support an electroactive biofilm that will work in an MEC is required.

2.5.3 Potential architectural innovation

There is the potential for these materials to be used for abiotic electrochemical applications. From the results generated from Chapter 2 alone, it is not possible to determine whether these materials are a viable electrode option for batteries (additional considerations, such as; packing, charge-discharge capability, etc. would be required). Manganese (IV) oxide has been applied in lithium-ion battery systems as a cathode replacement, support and lithium source (in the form of LiMnO_2 ,¹⁰⁵), but the lack of lithium on the electrodes tested means that the potential for an architectural innovative application to these applications cannot yet be confirmed. A more likely option for manganese (IV) oxide coated Carbisol M fibre materials could be as a material for super capacitors.¹⁰⁶

2.6 Summary

This phase of the project demonstrated that the recycled carbon fibre materials were usable in electrochemical applications. Furthermore, they were able to generate comparable currents to the graphite felt tested. The method used to electrodeposit the manganese (IV) oxide was also successful, with all materials (particularly the recycled carbon Carbisol M) having even coatings, in terms of coverage and thickness.

In terms of successful innovation, this phase of the work created a lot of potential for a usable and inexpensive anode material for use in an MEC. This potential was subsequently increased and arguably, confirmed in the next two phases of the project (Submissions 3 and 4, respectively), but this abiotic phase was useful for two reasons:

1. A rapid method of ascertaining whether there was any scope for using the recycled carbon by determining whether it could support electrochemical reactions on its anode surface.

2. By enabling other technologies that require conductive electrode materials. The use of the Carbiso M in batteries, supercapacitors or other fuel cells could help to drastically reduce their environmental footprint and economic cost.

With regards to MECs, this project generated two new research questions:

1. Can the recycled carbon fibre mats sustain an electroactive biofilm, suitable for a microbial electrolysis cell using wastewater as an inoculum?
2. Could a recycled carbon fibre electrode perform comparably to a commercial anode material that has demonstrated good performance in a microbial electrolysis cell?

3 Testing the potential anode materials in lab-scale MEC reactors

3.1 Abiotic performance does not always link to biotic performance

Graphite and carbon-based felts work very well as electrodes (or basis of electrodes) in fuel cells and battery systems. It is also true that they work well (or well enough) in MEC, MFC and other BES technologies.^{48,50,107} However, the use of virgin materials cannot be considered for larger-scale applications due to cost.^{67,79} The experiments in Chapter 2 showed that the materials derived from waste carbon fibre are able to conduct electricity and function in electrochemical systems at a significantly reduced cost to virgin graphite and carbon felts (with the added benefit of being significantly less impactful on the environment).¹⁰³ However, it was not confirmed at this stage whether these materials would function as anodes in MECs to support the proliferation of microorganisms or exoelectrogenic bacteria. Just because a material is conductive, it does not mean that it is conducive to use as an anode in an MEC (especially where capital costs are concerned). If these recycled materials are able to compete (and ideally outperform) the virgin carbon and graphite felts in terms of hydrogen recovery and wastewater treatment, then there will be a strong argument that their use in MEC (or MFC) technology will be innovative, due to the environmental benefits over the virgin materials as well as the large capital cost savings.

An understanding of the impact how the different materials or the presence of manganese (IV) oxide had on the community of the anodic biofilm was also important. Electrogenic microorganisms are the principal bacteria that oxidise the organic compounds within BES and higher abundances of these organisms have been linked to improved performances (higher currents, more hydrogen/power, etc.)^{46,108}.

3.2 Experimental setup – testing innovation

3.2.1 Materials

Four different anodes were tested in duplicate and the details were as listed in Table 3-1. Despite the earlier point of virgin graphite-based felts being unsuitable for large scale MEC technology, the same graphite felt material used in the abiotic tests in Chapter 2, was used as a control material, as it was confirmed as being functional for MEC technology.⁶⁷

Table 3-1: Anode materials used in the MECs tested in Chapter 3

<i>Cell number</i>	<i>Anode material</i>	<i>Coating</i>
1, 2	GFD 4.6	None
3, 4	M300	Manganese (IV) oxide
5, 6	M100	None
7, 8	M100	Manganese (IV) oxide

The cells had the same architecture described in chapter 2 and Figure 2-1. All anodes and cathodes were also the same size (4.5 cm²) and connected to a potentiostat (Dropsens 8000u) with 316 stainless steel wire current collectors (similar to the *Heidrich* and *Cotterill* pilots). The cathodes were manufactured from 316 stainless steel weldmesh with apertures of 1.3 cm² (PRW, UK), through which 1.5 g of 316 stainless steel wire wool was woven through (Merlin Motorsport, UK).

3.2.2 Operation

The MECs were fed with real wastewater that was collected twice a week post-settlement (before secondary treatment) from Finham wastewater treatment plant (Severn Trent, Coventry). The wastewater was pumped in at different flows of the course of the experiment to understand how the different systems responded to reducing hydraulic retention times (HRT). It has been reported that lower HRTs will be required for the larger-scale deployment of MECs to lower capital costs (as a smaller MEC would be required) and also reduce the operational costs (less time will be needed to treat the wastewater). HRTs of 10, 5 and 2 hours were used at different times, using peristaltic pumps (Watson Marlowe, UK) to control the flows and achieve the desired HRTs.

The cathodic chambers used a catholyte of 0.1 M NaCl, which have been used by *Cotterill et al* successfully.⁶⁷ Gas was collected from the cathodic chambers using “bubble displacement” tubes, which were custom made by the University of Warwick glassblower (Figure 3-1). These were inserted to the top of the catholyte chamber of the MEC using push-fit adapters.

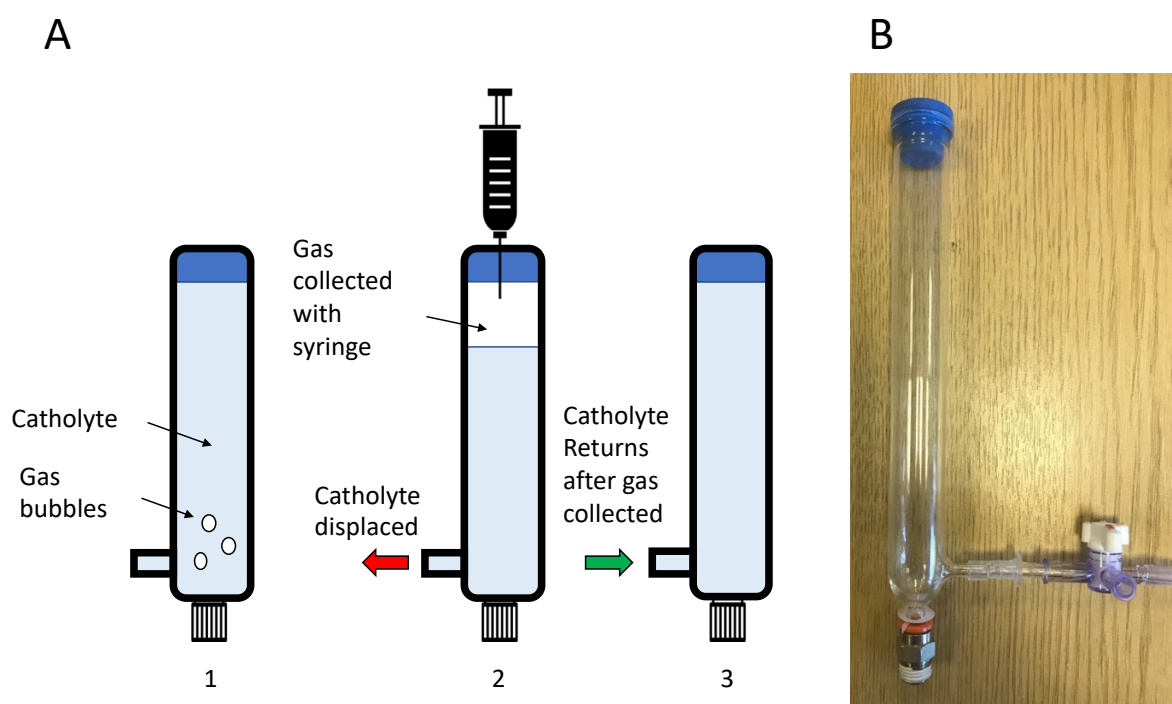


Figure 3-1: Gas collection tubes.

A: Representation of gas collection mechanism. B: Photograph of actual glass tube with push-fit adaptor.

The MECs were powered using a Dropsens potentiostat, fixing 0.4 V between the anode and the reference electrode for each MEC, allowing for the monitoring of only the anode performance in the system. This meant that any changes in current that are recorded are due to a change in electrochemical reactions occurring at the site of the anode (e.g. resulting from microbial activity). This did have the downside of not knowing the voltage and/or power input to the system, as would be the case with a two-electrode system.

3.2.3 Parameters measured

The parameters measured were; hydrogen gas production (volume and concentration), wastewater treatment performance (COD removal) and current generation. Gas chromatography was used to analyse the gas produced by the MECs.

Gas was collected from the MECs and analysed for purity by gas chromatography (Agilent Micro GC). The GC was calibrated with a 5-point calibration using pure H₂ from Calgass. The volume of gas produced was measured using gas -tight borosilicate syringes which were also used to withdraw the samples for GC injection.

Chemical oxygen demand (COD) tests were conducted using HACH-Lange cuvettes. The influent was measured using LCI-400 (0-1000 mg L⁻¹) and effluent using LCK-314 (15-150 mg L⁻¹) test sets. A HACH-Lange reactor a HACH-Lange spectrophotometer (DR2800) were used to determine the concentrations. The spectrophotometer was calibrated using a 300 mg L⁻¹ COD HACH-Lange standard solution.

Electrical energy (ηE), coulombic (CE), and substrate efficiencies (S_E) were calculated to help assess the performance of the different anode materials. The equations used are detailed below:

$$\textbf{Equation 3-1: } \eta E = \frac{W_{out}}{W_E}$$

$$\textbf{Equation 3-2: } CE = \frac{N_{CE}}{N_{H2}}$$

$$\textbf{Equation 3-3: } S_E = \frac{N_S}{N_{H2}}$$

The extra steps and theory required to calculate the efficiencies are detailed in the appendix (Section 8.1.2). These efficiencies are very useful to understand where losses in the system may be occurring and provide explanations for low recoveries of hydrogen (or other products).⁴⁴ A low energy recovery efficiency suggests that of the available input energy the rate of hydrogen gas is not covering the energy use to run the system and in some cases, too high a voltage is being applied, suggesting that a lower voltage would yield the same performance but at an improved efficiency.⁴⁷ Low coulombic efficiency suggests hydrogen gas loss (possibly due to leakage or consumption by hydrogenotrophic bacteria). Low substrate efficiency also suggests low recoveries, but if the recovery is high while the overall substrate (in this case COD) removal is low, this suggests that the limiting factor could be due to a lack of substrate oxidation at the site of the anode.

3.2.4 SEM protocol

SEM was conducted on samples of the anode. The samples required a fixation protocol of; 24-hour soak in refrigerated 2.5% glutaraldehyde (in PBS), followed by dehydration stages using increasing concentrations of ethanol (25%, 50%, 75%, 100% and a final 100% of ethanol anhydrous). The samples were then airdried and sputter-coated (Cressington) with a gold-palladium alloy and viewed under SEM (Hitachi Desktop SEM).

3.2.5 16S sequencing of the biofilms on the anodes

DNA extraction on three samples from each anode was also conducted using a soil DNA extraction kit (MP biomedical, USA). The samples were acquired by using a 0.5 cm diameter steel hole-punch. Post extraction, the samples were then prepared by Queen Mary University for sequencing (16S rRNA gene). The DADA2 script was then used to process the data to assign taxonomy to Genus level for detected sequences.

A Simpson Index of diversity provides a value between 0 and 1, where 1 indicates a very high level of biodiversity and was used to assess the diversity of the community.^{109,110} A Shannon diversity index was used as an additional test for the overall diversity measurement of the system.¹¹¹ Both are valid tests to use, but can respond in different ways to different data, where a Shannon diversity index is most affected by changes in the importance of the rarest taxa whereas Simpson index of diversity is most affected by changes in the abundance of the most common taxa.¹¹² The investigations in the taxonomy of the biofilms was to establish whether the materials had any significant differences in the microbiological communities and whether this correlated to the performance of individual MECs and/or the anode material used.

3.3 Results of the lab-scale tests

3.3.1 Recycled carbon fibre materials do work as anodes for MECs

The main aim of this phase of the study was to confirm whether the chopped waste carbon mats would suffice as anodes for MECs. The question that needed answering

was: would the voltage supply from the potentiostat be spread over the fibres to a sufficient extent which would allow for a biofilm to grow?

All of the MECs successfully reduced the COD content of the wastewater, produced changes in their current generations (dependent on organic loading rate and time) and produced some hydrogen gas. The MECs using the less expensive and more environmentally sustainable recycled carbon fibre materials as anodes were all able to sustain an electro-active biofilm.

3.3.2 Wastewater treatment efficacy

All of the MECs were able to significantly reduce the chemical oxygen demand level (COD) of wastewater, to a standard where the wastewater was clean enough to be returned to the environment (below 125 mg L⁻¹ based on the UWWTD) (Figure 3-2), although it is unknown whether the other pollutants of the wastewater were low enough for safe discharge (e.g. phosphorous, ammonia, suspended solids, etc.). Expected oscillations in the quality of wastewater treatment were observed; for example, when a wastewater influent had a higher COD concentration, the effluent COD was also higher, when compared to an influent with a lower COD concentration.

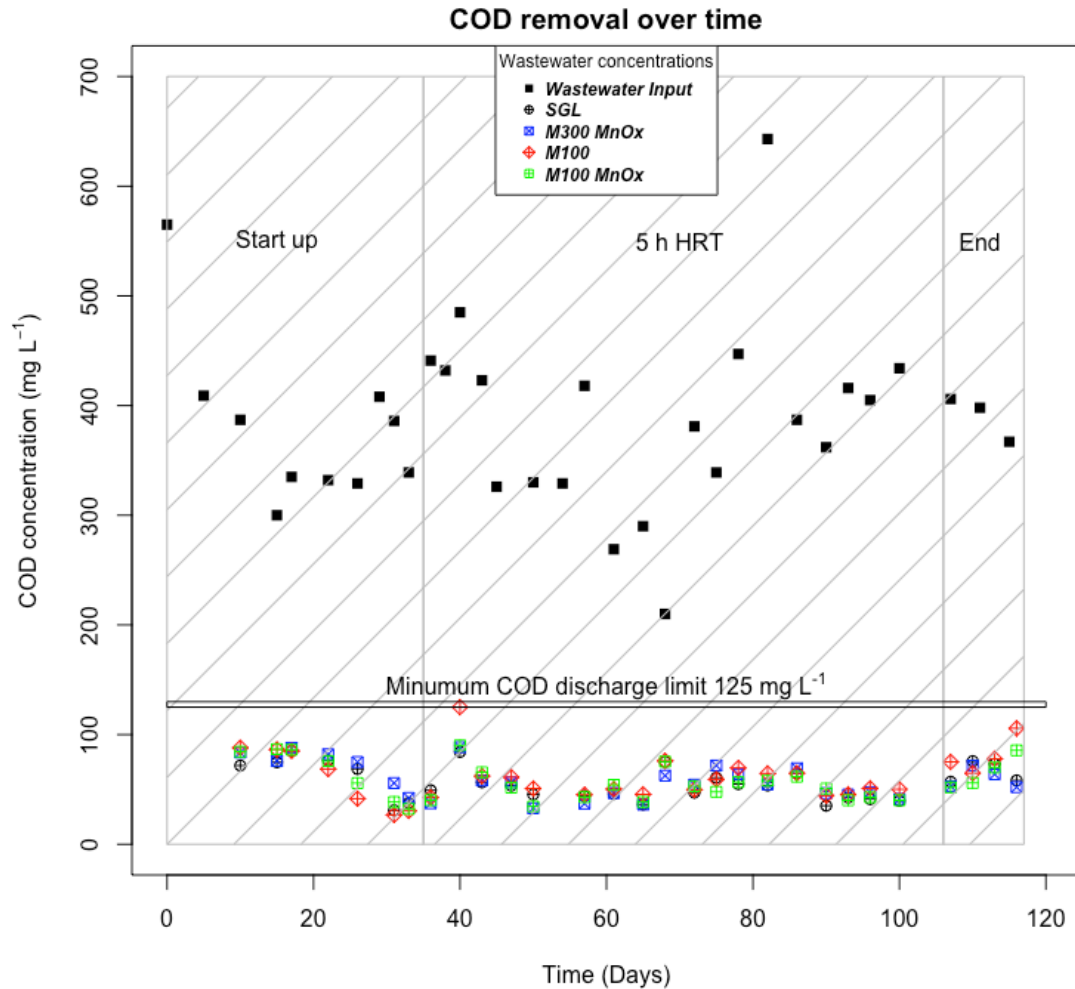


Figure 3-2: Overview of the change in COD levels from the input wastewater to the output effluents over time.

Increases of COD in the effluents were also observed with a reduction of the hydraulic retention time (HRT); observable between the last HRT 10 COD measurements and the first HRT 5 measurements (Day 37-40) and over the two 2h HRT periods (Days 107-109 and 113-116 - Figure 3-3 and Table 3-2).

Table 3-2: Average COD inputs and outputs by HRT

		Wastewater COD concentration by origin (mg L ⁻¹)				
HRT average		SGL 4.6 output	M300 MnOx output	M100 output	M100 MnOx output	WW input
	Total	56.55	58.64	62.57	57.81	385.70
	HRT 10	61.22	67.27	59.82	62.98	358.33
	HRT 5	52.12	53.68	60.56	53.10	381.30
	HRT 2	74.53	67.78	91.83	77.83	420.00

Despite the increases in flow rate, the output of COD was still below the 125 mg L^{-1} required for safe discharge. All of the materials produced their best quality effluent at different timepoints, shown in Figure 3-3.

Batch and 10-hour HRT - Start-up phase

The MnOx coated M300 had the highest number of instances where the COD was highest (5), with the uncoated plain M100 having the lowest COD four times. Throughout the 10 hour HRT phase, the average effluent quality did increase, as the COD concentrations reduced constantly, even with an increasing concentration of COD in the influent wastewater (Figure 3-3: Start-up plot).

5-hour HRT – Mid phase

COD concentrations of all the effluents increased considerably and in the case of the M100 by more than double (Figure 3-3: day 40 – Mid Phase Plot). From this point onwards, the M100 produced the worst effluent in the majority of COD tests. The manganese (IV) oxide coated materials performed better in this phase when compared to the SGL felt, producing effluents that were better or marginally worse. All materials tested showed high percentage removals of COD from the wastewater, with the lowest percentage removal being the M100 with an overall average (the entire 120-day experiment) of 83.23% and the graphite the highest with 84.62%.

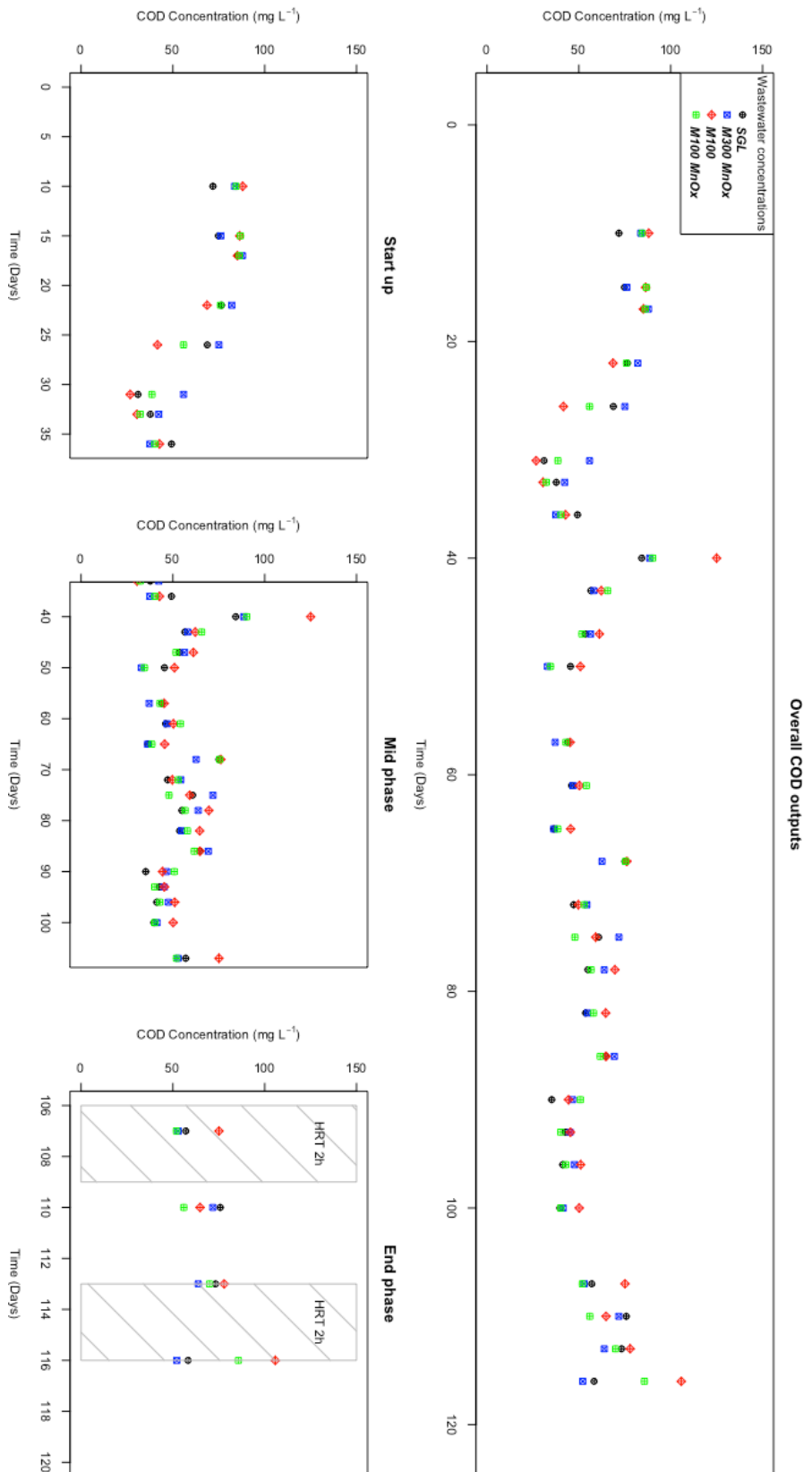


Figure 3-3: Average MEC effluent concentrations excluding the input values.

An overall COD output is shown, as well as snapshots of the three key timestamps of the experiment; the start-up, mid phase and end phase (where the two HRT 2-hour windows are highlighted).

2 hours HRT – End Phase

Higher flow rates resulted in poorer quality effluents (higher COD concentrations) but also produced larger differences between the MECs in terms of COD removal (Figure 3-3 – End Phase plot). The MnOx coated M300 and graphite were both comparable (with the M300 MnOx marginally better) while both being significantly better than the M100 materials (both plain and MnOx coated).

Overall wastewater treatment efficacy

A summary of the number of times an MEC with a particular material produced the worst or best effluent in terms of COD content can be found in Table 3-3. The difference is very small, suggesting that the far less expensive materials (M100, M300 MnOx and M100 MnOx) can match the graphite felt. The only point at which the M100 performed best was during the 10 hour HRT period, hence why it was ranked first (green colour) in terms of COD removal (Table 3-3).

Table 3-3: Comparison of the average % reduction of COD by MECs using different anode compositions.

By row: The “greener” the highlight the higher the ranking and the “redder” the highlight the lower the ranking. The legal discharge limit according to the 1994 wastewater treatment directive requires a minimum 75% COD reduction from the original influent.

Duration	% of COD reduction in effluent wastewater			
	Graphite	M300 MnOx	M100	M100 MnOx
Overall	84.62	84.14	83.23	84.41
HRT 10	82.15	79.88	83.20	81.74
HRT 5	85.68	85.64	83.75	85.60
HRT 2	81.33	82.33	73.95	78.90
From high inputs	84.83	85.94	81.41	84.84

The M100 anodes had the lowest mass per unit area (100 g m^{-2}) and they also had the worst performance in terms of COD removal. The reason for this is likely due to the lower amount of carbon fibre that was available for colonisation by a biofilm, resulting in a reduced rate of wastewater treatment during the experiment. This is particularly evident for the lowest HRT of 2 hours, where the effluent from the M100 MECs had 8% higher COD compared to the M300 MnOx. This reasoning is also supported by the higher input time point as the M100 MECs still had the lowest COD removal (when the input COD was 643 mg L^{-1} on day 82 – all data available in the Appendix, Table 8-2). Manganese (IV) oxide has enhanced the performance of the

MECs concerning wastewater treatment as the same M100 material with the coating performed 5% better during the HRT of 2 hours and 3% better during the period of higher COD input from day 82.

With regards to the availability of surface area of fibres for the biofilm growth and therefore, active area for wastewater treatment, the graphite felt had the highest mass and therefore would be expected to have significantly better performance than the M100 materials, with and without Mn (IV) oxide. On average, the graphite felt did perform better than both, over 7% more COD removal than the plain M100 but less than 3% COD removal than the M100 with MnOx. When considering the fact that the graphite felt was over 4x the mass of the M100 and is far more expensive per unit area, with the base materials graphite felt costing over £85 per m² more than the M100 (cost comparisons are explored in detail in Section 5.2), this is a promising result for the recycled carbon fibre, especially when considering that the thicker recycled carbon fibre (M300) that was coated with Mn (IV) Ox performed better than the graphite during the higher organic loading rate periods (2 hour HRT and the 638 mg L⁻¹ high input period), suggesting that the increased thickness of the M300 MnOx over the M100 MnOx had a positive impact on performance, due to the increased amount of biofilm proliferation possible due to the increased available surface area for bacterial growth.¹¹³

Despite the positive results of the recycled carbon fibre (namely that they served to remove COD and therefore treat wastewater), the differences in performance of the MECs was not found to be statistically significant from Anova analysis in terms of concentration of COD in the effluent ($P=0.551$). This was mirrored for the material averages ($P=0.587$). Therefore, the different anode materials did not result in a statistically significant performance difference in terms of COD removal.

3.3.3 Hydrogen recovery

There was very little gas collected in the glass tubes throughout the experiment and the gas collected had low purity. There was also a failure of the GC mid reading which resulted in a loss of data (detailed below).

Volume and moles of hydrogen

The first gas bubbles visible on the cathodes were seen shortly after the increase of flow (reducing the HRT from 10 to 5 hours). The increased organic loading rate (OLR) that this flow rate caused triggered the gas production (day 37), suggesting that the 10-hour HRT was not providing sufficient substrate for gas production, even though BESs have the potential to function in lower strength wastewaters.¹¹⁴ It is likely that the gas was being produced in such small quantities that it was being lost via leakage and hydrogenotrophic taxa.¹¹⁵ Sufficient collectable gas in the tubes was collectible for a GC measurement on day 67, as the production of gas would have been high enough to result in collection in the gas tubes. The majority of the gas collected at this first time point had no detectable hydrogen (MECs 1,2,5,6 and 7). This included both the SGL 4.6 based anodes, the uncoated ELG M100 anodes and one of the manganese (IV) oxide coated M100 anodes. The three MECs that produced hydrogen gas were the recycled carbon materials coated with manganese (IV) oxide: MECs 3 and 4 (M300) and MEC 8 (M100).

The quantity of gas produced was very low when considering the theoretical recoverable amount from the organic compounds fed into the reactor. During the 4 months of operation, the total amount of oxygen required to oxidise the organic compounds (i.e. total COD) in the wastewater is estimated to have been 196 g. As 1 g of COD equates to 0.065 M of H₂, there was a theoretically 12 mol of H₂ available for recovery from each reactor (this was calculated using the data in the appendix in Table 8-1). The calculated molar recoveries for each reactor are detailed in Table 3-4.

Table 3-4: Total mM H₂ recoveries per MEC.

MEC	Anode Material	Total volume of gas (mL)	Total H ₂ (mM)	Ranking
1	SGL 4.6	4	0.0270	3
2	SGL 4.6	8	0.0505	2
3	M300 - MnOx	15	0.1865	1
4	M300 - MnOx	11	0.0193	5
5	M100	4	0	6=
6	M100	7	0	6=
7	M100 - MnOx	11	0	6=
8	M100 - MnOx	12	0.0231	4

*Highlighted numbers had second round of hydrogen readings lost due to a failure of the GC mid reading.

The low level of hydrogen production across all of the MECs would have effected by the more complex nature of the wastewater substrates available to the biofilms in the MECs, whereas more simple feeds (i.e. a single sugar type such e.g. sodium acetate, glucose) result in much higher current densities and hydrogen recoveries.¹¹⁶ The HRTs for these MECs were also quite low, relative to other smaller-scale lab tests, meaning the combination of a fast flow rate, complex (and changing) substrate mix at a lower concentration would have impeded the overall recovery of hydrogen gas.⁴⁸

In terms of the volume of gas produced, the electrodeposition of manganese (IV) oxide had a positive impact. The plain M100 materials produced a combined total of 11 mL of gas, whereas the M100 (MnOx) anodes produced 23 mL – over twice as much. The M300 MnOx produced marginally more gas than the M100 MnOx (26 mL) which suggests that in relation to hydrogen production, the limiting factor was not the anodic surface area, similar to how it appears to have been for the COD removal performance. The mass of the M300 is three times that of the M100, yet the gas productions were very similar. The graphite felt was worse than both the M100 MnOx and M300 MnOx, whilst having the highest amount of mass per unit area, further supporting the claim that it was not anodic surface area or mass that was rate-limiting for hydrogen gas production. Thicker anodes have been demonstrated to increase performance in MFCs due to the reduced oxygen availability at the innermost point of the anode, which could explain the small difference in gas production between the M300 MnOx and M100 MnOx but the difference is so small that this seems unlikely as the explanation.¹¹⁷

However, Anova statistical tests demonstrated that the differences in the means of gas produced from each MEC (as volumes) was not significant ($P=0.613$). This was further confirmed when the same anode materials gas productions were summed and the same Anova test was repeated ($P=0.568$). These two results for the analysis of variance mean that the hypothesis that the anode material would result in a significantly different gas production can be rejected and the null hypothesis is accepted (that there are no differences in gas production due to anode material selection). N.B. this null hypothesis is accepted for this particular experimental set up.

3.3.4 Current generation

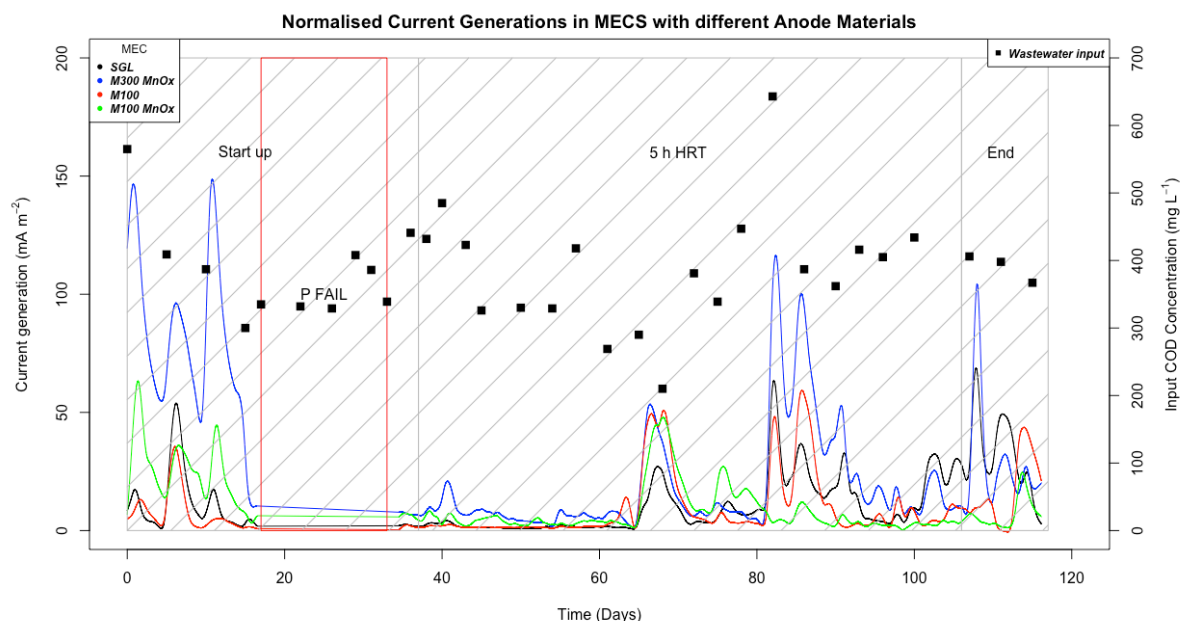


Figure 3-4: Average current generation during the 116 days of operation with the COD influent.

Focus points of the start-up, 5-hour HRT period and end phase. The red box indicates the point at which the potentiostat lost data (P FAIL).

The initial current dropped during the batch phase, until the flow-through mode started (Day 5), with a continuous downward trend. Through the 10-hour HRT period (Day 5 to 37) the current remained low post the sodium acetate consumption from the batch phase. It has been reported that higher currents are possible when the feed is less complex, explaining the higher initial currents which then fell to comparatively low levels.¹¹⁶ The 5-hour HRT initiation yielded a small increase in current which, remained low and did not continue to increase over time. It is possible that the organic loading rate was still not sufficiently high enough to generate higher currents or enable for increased biofilm proliferation (which would be signalled by increasing currents).¹¹⁸ The pump tubing change at day 60 caused an increase in current for all MECs, likely due to the improved delivery of organic compounds for breakdown by the microorganisms (Figure 3-4). To ensure effective delivery of organics to the MECs, the tubing would have benefited from a weekly change, as the tubing had a tendency to be deformed after long periods of use.

A large increase in current (average between the same anode materials) was observed for the graphite and manganese (IV) oxide coated M300 anodes, following

delivery of a high strength wastewater at day 82 (Figure 3-4). The spike in current was due to an increase in electron transfer from the biofilm to the anode, likely due to the increased proliferation of microorganisms due to the higher availability of organic compounds for feeding, which was to be expected as higher concentrations of substrates do increase the current generation of BES.¹¹⁶ This coincided with a higher rate of gas collection from all tubes, in particular for the manganese (IV) oxide coated recycled carbon fibre materials and the untreated SGL graphite felt. Following this higher input of COD, the average current was considerably higher for all MECs until the close of the experiment, indicating that a proliferation of microorganisms on the anode had occurred.

Despite the higher produced currents, a deterioration of current was observed. The HRT was reduced to 2 hours and the high current generation was replicated again. The high flow rate would ideally have been maintained, but due to the lack of space for storing the wastewater and issues with health and safety to collect wastewater every day from the plant (and at higher volumes), the 2 hour HRT could not be maintained for more than 3 days, and as expected, spikes in current were observed for all MECs (Figure 3-4 – end phase). The 2-hour HRT increased the organic loading rate of the system, providing more substrate for the biofilms to oxidise, which increased the current of all MECs. This demonstrated that the recycled carbon fibre anodes, like the graphite felts, were able to sustain biofilms and support the proliferation of the microorganisms. The overall current generations were unexpectedly low for all of the systems, but the MnOx M300 anodes which were significantly less expensive than the graphite (as well as being significantly more sustainable)¹⁰³ still generated higher currents from microbial activity.

The uncoated M100 had the lowest current generation but did respond to the higher organic loading rates. The manganese (IV) oxide coated M100 was consistently better in terms of the current generation, indicating that the coating was having an impact on the current generation when operated with a potentiostat. The reason for the higher current will not likely have been due to an increase in resistivity, as the opposite should have occurred. Manganese (IV) oxide deposition would have increased the resistivity of the M100 so if there has been an increase in current, it will likely have been due to the microbial activity, assuming that no changes occurred to the cathodes (the impact

the microbial taxa had is discussed in section 3.3.9). The current generation from the manganese (IV) oxide coated M100 was both higher and lower than that of the SGL at different time points. The lower current generations of the M100 MnOx compared to the M300 MnOx were expected as the M300 variant is approximately three times the mass and should, in theory, have three times the surface area and higher surface area anodes tend to increase the current generation of MECs due to the potential for increased biofilm which can oxidize more substrate.

3.3.5 Electrical energy recovery

The electrical energy recoveries for all of the MECs were very low due to the low hydrogen recovery and relatively high energy input, determined by using the Butler Volmer equations detailed in the Appendix (Section 8.1). As the energy input would have been high (due to a set voltage of 0.4 V between the anode and the reference) the potential efficiencies would have been very low, even with high recoveries of hydrogen gas. At 1 V (set between the anode and cathode) the maximum energy recovery efficiency is 123%, assuming maximum hydrogen recovery.⁴⁷ The efficiencies and their relative rankings are shown in Table 3-5. The ranking of MEC 1 in first is due to the significantly lower current generation compared to MEC 3, meaning that MEC 3. Despite MEC 3 having approximately 7 times more hydrogen than MEC 1, the overall η_E is still lower as MEC 3 should have recovered more hydrogen relative to the generated current. All of the MECs therefore could have been operated at a lower voltage and would likely have generated the same volume of hydrogen gas.

Table 3-5: Electrical energy recoveries for the MECs

MEC	Material	η_E (%)	Ranking
1	SGL 4.6	0.110	1 st
2	SGL 4.6	0.042	3 rd
3	M300 MnOx	0.080	2 nd
4	M300 MnOx	0.015	5 th
5	M100	0.000	=6 th
6	M100	0.000	=6 th
7	M100 MnOx	0.000	=6 th
8	M100 MnOx	0.022	4 th

3.3.6 Coulombic efficiency

The coulombic efficiencies (CE) for all MECs were less than 0.1% which, due to the effective wastewater treatment observed, is assumed to be due to leaks in the gas collection tube and the reactors themselves. Rankings have been applied to more clearly differentiate the systems performances in this metric, but it is evident that major losses were occurring in all of the systems. It is also likely that hydrogenotrophic microorganisms have proliferated on the cathodes, resulting in the consumption of evolved hydrogen gas which has been reported in multiple MECs of different scales.^{67,115,119} Changes to the architecture to collect more gas and a reduction of the internal resistance of the system would improve hydrogen recovery and therefore, the coulombic efficiency.¹²⁰

Table 3-6: Comparison and rankings of coulombic efficiencies of the 8 MECs.

MEC	Material	N _{H2} (mM)	CE (%)	Ranking
1	SGL 4.6	0.027	5.01E-02	4 th
2	SGL 4.6	0.051	1.28E-01	3 rd
3	M300 MnOx	0.186	6.50E-02	5 th
4*	M300 MnOx	0.019	3.45E-01	1 st
5*	M100	0.000	0	=6 th
6*	M100	0.000	0	=6 th
7*	M100 MnOx	0.000	0	=6 th
8*	M100 MnOx	0.023	2.46E-01	2 nd

Samples labelled with * could not be evaluated due to problems with the gas chromatograph.

3.3.7 Substrate efficiency

The total recovered hydrogen is very low when compared to the theoretical recoverable amount from all MEC (greater than 99.9% losses - Table 3-7).

Table 3-7: Substrate efficiencies for the MECs

	MEC 1	MEC 2	MEC 3	MEC 4	MEC 5	MEC 6	MEC 7	MEC 8
Average removal (%)	84.17	84.47	83.63	83.84	82.63	82.78	85.00	83.32
Removed (g)	8.25	8.28	8.20	8.22	8.10	8.11	8.33	8.16
H ₂ theoretical (mM)	0.52	0.52	0.51	0.51	0.51	0.51	0.52	0.51
H ₂ actual (mM)	0.03	0.05	0.19	0.02	0.00	0.00	0.00	0.02
SE (%)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

This was observed for all materials, including the SGL 4.6 graphite felt control.⁶⁷ As has been stated in the previous wastewater treatment analysis section (Section 3.3.2), the overall COD removal was very high which should have resulted in a greater production of hydrogen (there were a theoretical 0.51-0.52 moles of hydrogen available). Based on the lower SE of the systems, a fundamental failing of the systems is apparent, likely brought about the leakages, hydrogenotrophic microorganisms and an architectural problem with the gas collection vessel.

3.3.8 Microbiology - SEM

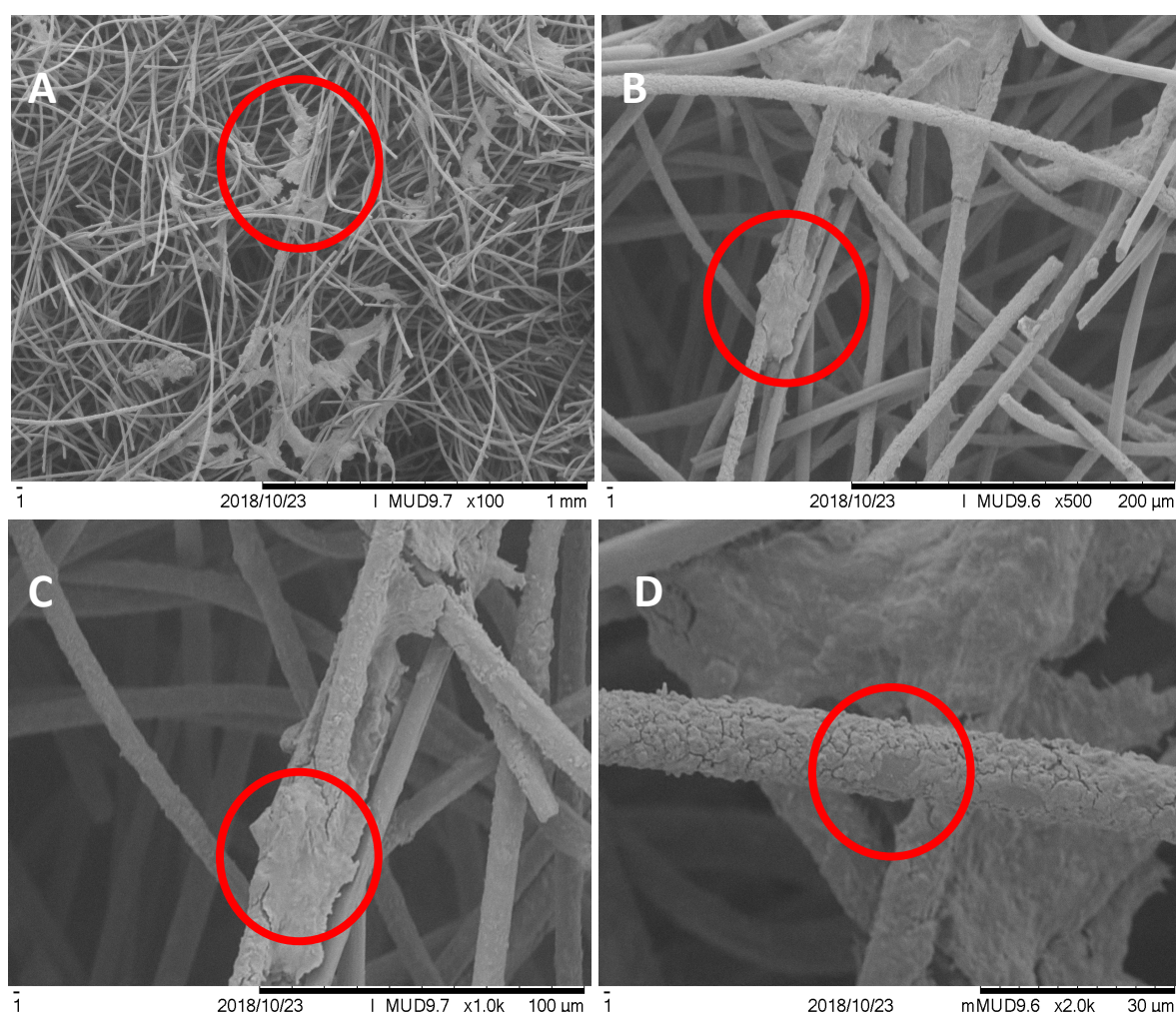


Figure 3-5: SEM images of GFD felt anodes after three months of operation SEM magnification at 100x (A), 500x (B), 1000x (C) and 2000x(D). Circles show areas of dense biofilm.

The SGL GFD 4.6 had good coverage of biofilm (Figure 3-5) with vast areas of whole fibres being completely coated by biofilm. The biofilms appeared relatively

homogenous, though individual cells at the level of magnification analysed was not possible. As this is the ‘control’ material (confirmed as a material that has been functional as an MEC anode)⁶⁷ it was important to confirm the presence of a biofilm, to allow for comparison to the recycled carbon fibre materials.

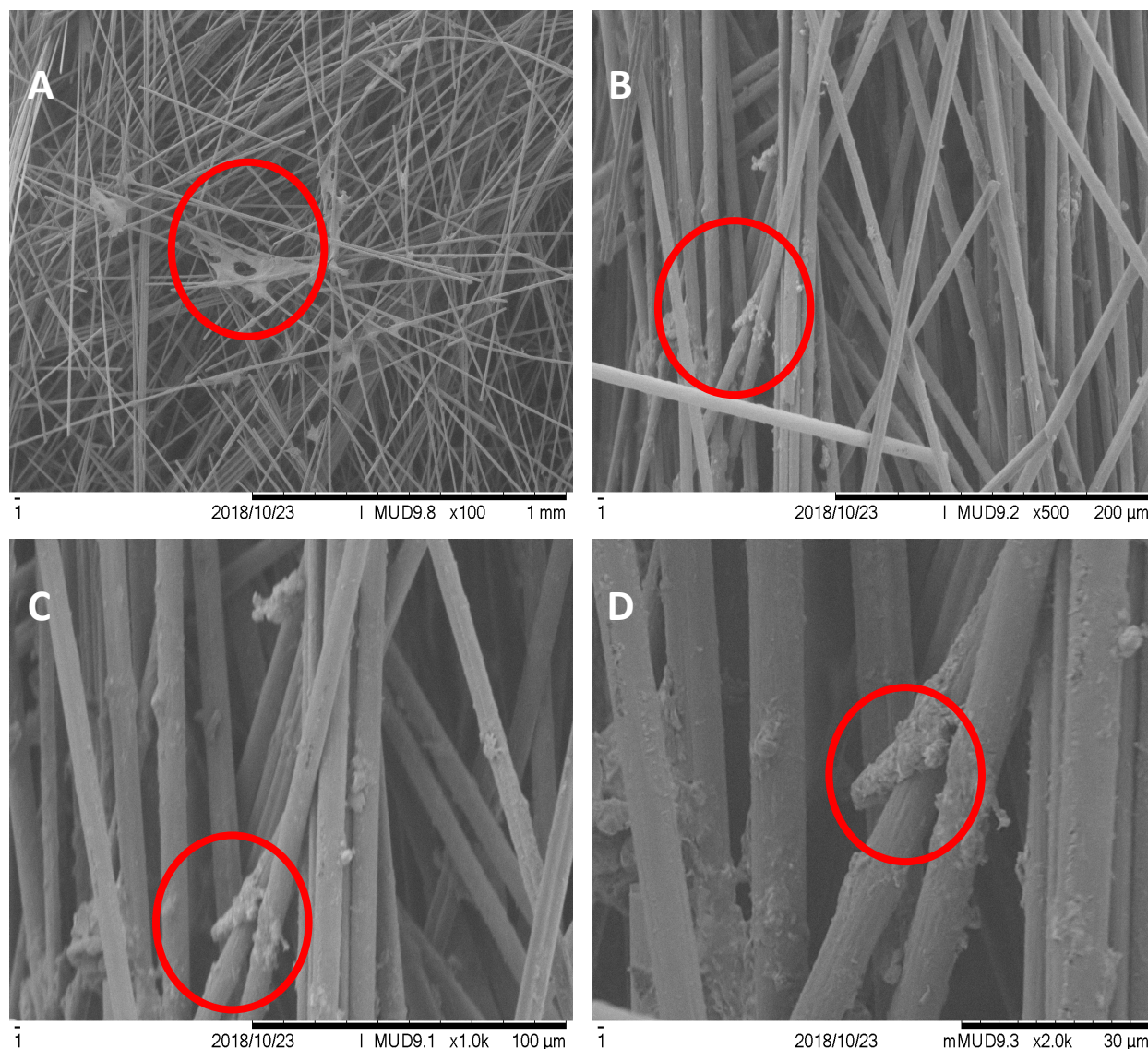


Figure 3-6: SEM images of M Carbis M100 carbon fibre anodes after 4 months of operation.

SEM magnification at 100x (A), 500x (B), 1000x (C) and 2000x(D). Circles show areas of dense biofilm

The uncoated M100 (Figure 3-6) had little visible biofilm when compared to the graphite felt anode. There appeared to be small patches or “clusters” where a biofilm had developed, but not to the level of the manganese (IV) oxide coated anodes or the graphite. This correlated with the lower current densities recorded, as well as the lower

level of wastewater treatment and hydrogen gas production during the mid-point and end of the experiment (See section: 3.3.4).

When comparing the uncoated M100 (Figure 3-6) to the coated M100 (Figure 3-7), there appears to have been a significant difference in the formation of biofilms. At all levels of magnification, a relatively homogenous coating of biofilm is visible (the granular/rougher surface texture). Crucially, the manganese (IV) oxide coating (the smoother areas of the fibres) is still visible on the fibres, suggesting that the coating was stable during the MECs operation, surviving both the voltage application and the conditions of the wastewater.

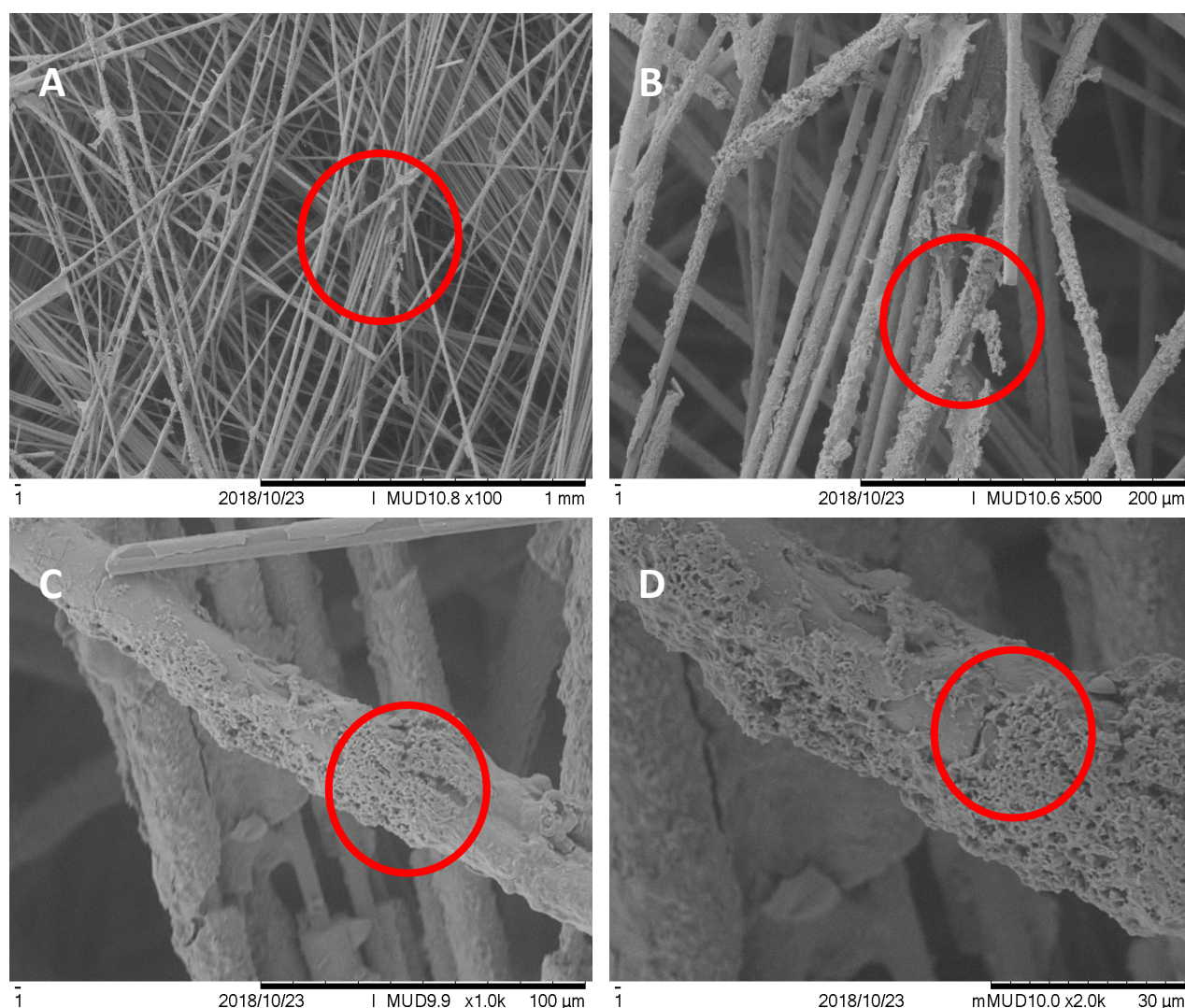


Figure 3-7: SEM Images of MnOx coated ELG M100.

SEM magnification at 100x (A), 500x (B), 1000x (C) and 2000x(D). Circles show areas of dense biofilm.

The addition of manganese (IV) oxide to the M300 material (Figure 3-8) appeared to have also positively influenced the growth of biofilms – the biofilms look similar to those visualised on the M100 anodes that were coated with manganese (IV) oxide (Figure 3-7). It was not expected that the overall thickness/appearance of the biofilm would have overly different between the MnOx M100 and the MnOx M300 as they are both the same material but with different thicknesses.

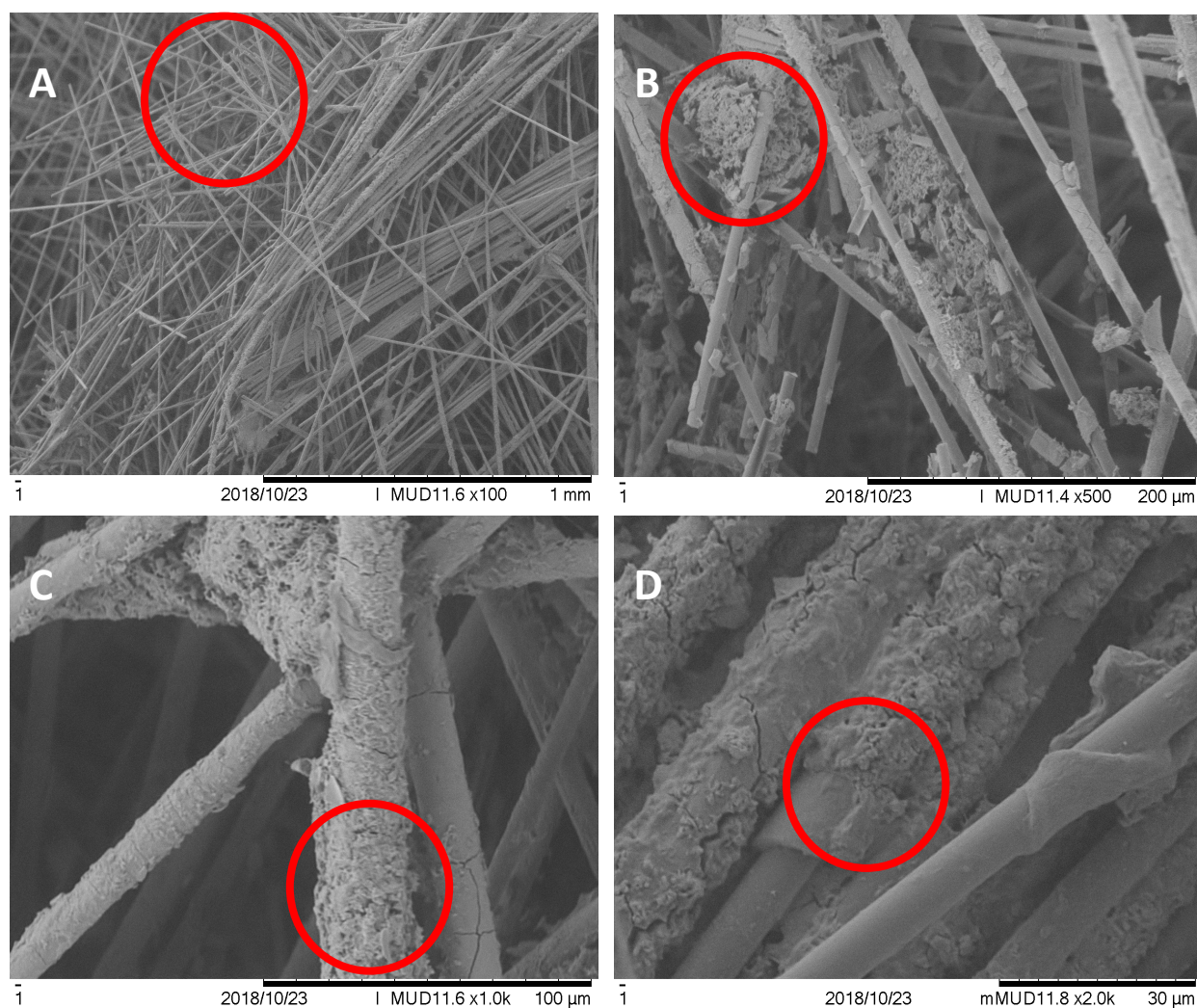


Figure 3-8: SEM of Manganese oxide coated M Carbiso M300 fibres

SEM magnification at 100x (A), 500x (B), 1000x (C) and 2000x(D). Circles show areas of dense biofilm.

3.3.9 Microbiology - DNA Analysis

Higher abundances of exoelectrogenic bacteria have been shown to correlate positively with better performances of MFCs and MECs.⁴⁶ As MECs are operated under anaerobic conditions, the species of microorganisms that are enriched tend to be obligate anaerobes including; *Geobacter spp.* (in particular, *Geobacter sulfurreducens*) which are known exoelectrogenic microorganisms found in wastewater sources and have been studied extensively for their performance in both MFCs and MECs.^{47,121–124} *Pseudomonas spp.* and *Shewanella spp.* are other examples of known exoelectrogenic microorganisms that have been identified in the biofilms of anodes used in MECs, generating high current generations under certain conditions (*Shewanella spp.* requiring low oxygen conditions for example).^{46,125} Therefore, of particular interest were any differences in the abundances of known exoelectrogens between the different anodic biofilms.

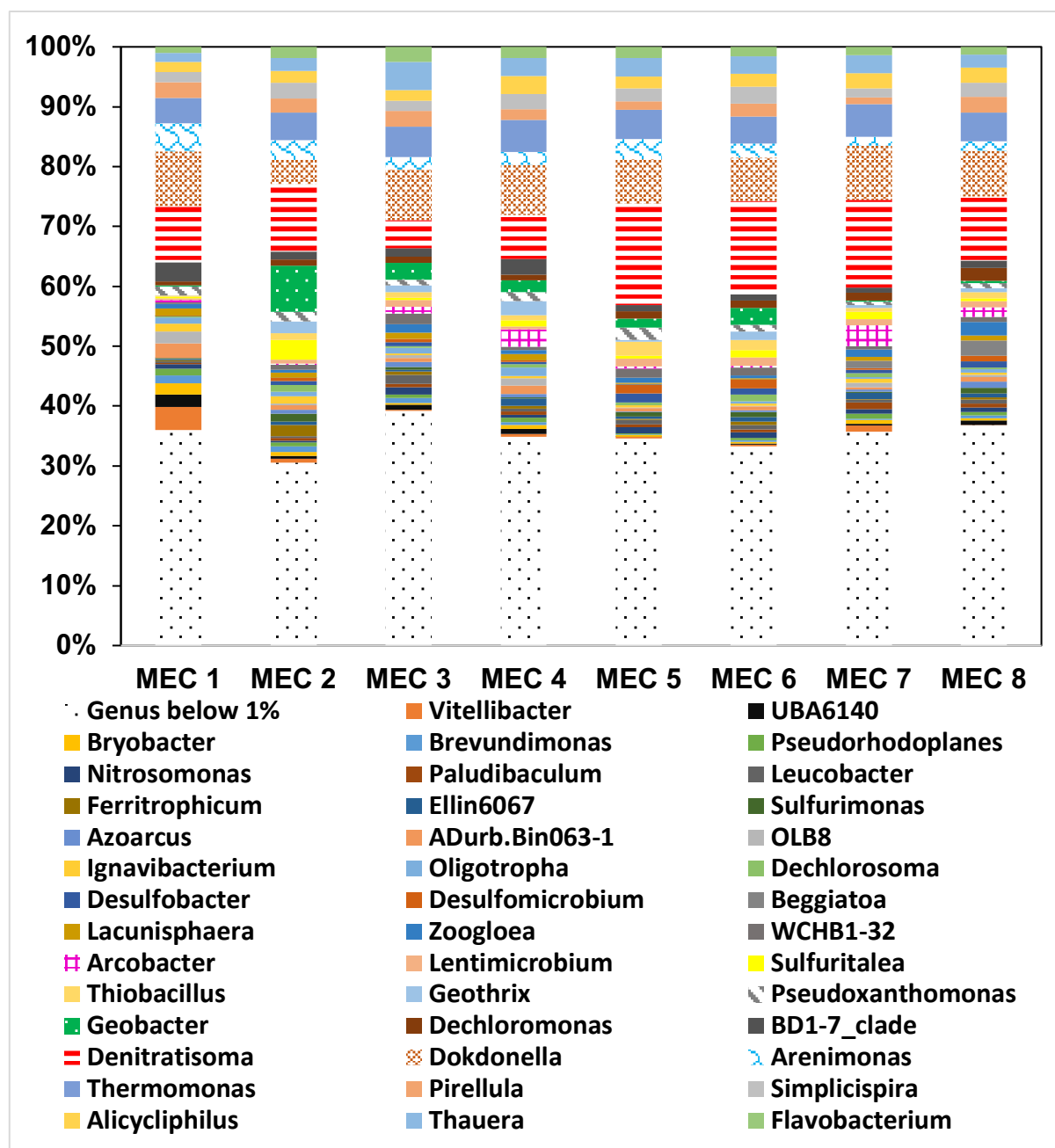


Figure 3-9: Stacked bar plot comparing genus relative abundance that was over 1% on the anodes of the different MECs.

The DADA script was able to identify the microorganisms to genus level, believed to be due to the shorter amplicon lengths (approximately 270 bp). An overview of the different genera with a relative abundance of over 1% are shown in Figure 3-9. It is clear that there were differences in abundance between certain genera between the different MECs, namely *Geobacter* and *Arcobacter*. The possible significance of these two differences was then investigated further, but of note, from this figure alone was very difficult to ascertain differences in sulfate reducing bacteria or other lower

abundance exoelectrogens (N.B a list of all abundance values for genera above 1% in the MECs is available in the Appendix Table 8-2).

Geobacter genus abundance was negatively affected by the presence of manganese (IV) oxide, demonstrated by the higher abundance of the genera identified in the biofilms of the uncoated M100 anodes relative to the manganese (IV) oxide coated M100 anodes (Table 3-8).

Table 3-8: Percentage abundance for *Geobacter*, *Arcobacter* and all SRB genera

	MEC 1	MEC 2	MEC 3	MEC 4	MEC 5	MEC 6	MEC 7	MEC 8
<i>Anode Material</i>	Graphite	Graphite	M300 MnOx	M300 MnOx	M100	M100	M100 MnOx	M100 MnOx
<i>Average normalized current (mA m⁻²)</i>	19.31	92.73	172.95	95.09	31.88	24.35	44.69	81.47
<i>Gas Volume (mL)</i>	4	8	15	11	4	7	11	12
<i>Geobacter (%)</i>	0.15	7.73	2.75	2.01	1.56	2.81	0.16	0.40
<i>Arcobacter (%)</i>	0.35	0.18	1.19	2.92	0.34	0.29	3.51	1.56
<i>Shewanella (%)</i>	<0.01	<0.01	0.30	0.07	<0.01	0.00	0.04	0.03
<i>SRB (%)</i>	0.26	2.80	2.48	1.34	5.10	5.05	1.43	3.04

This did not seem to be detrimental to the performance, as the manganese (IV) oxide coated M100 performed better than the plain, despite the lower abundance of *Geobacter* genus. This was surprising as higher abundances of *Geobacter* spp. tend to positively correlate with better performances in BES when in a mixed culture (not with a monoculture of *Geobacter*).¹⁰⁸ MEC 2 (using a graphite anode) had the highest abundance of *Geobacter* genus (7.73%) believed to be attributed to the lower resistivity of the graphite felt, compared to the recycled carbon fibre materials. This was not replicated in MEC1, which also used the graphite felt anode but demonstrated a very low abundance for the same genus. As a similar trend for the sulfate reducing bacteria (SRB) genera (e.g. *Desulfovibro*) was observed for MEC 1 it's possible that a leak allowing oxygen into the system occurred. This would be a justification for lower abundances of both SRB and *Geobacter* genus as they are obligate anaerobes (obligate anaerobes being taxa that only grow in the absence of oxygen).¹²⁶

There was not a clear correlation between a higher abundance of *Geobacter* and current generation in this experiment (Figure 3-10), most notably for MEC 2 which had the highest abundance of *Geobacter* (7.73%) but was not the best performing MEC in terms of current generation or hydrogen recovery (Figure 3-10).

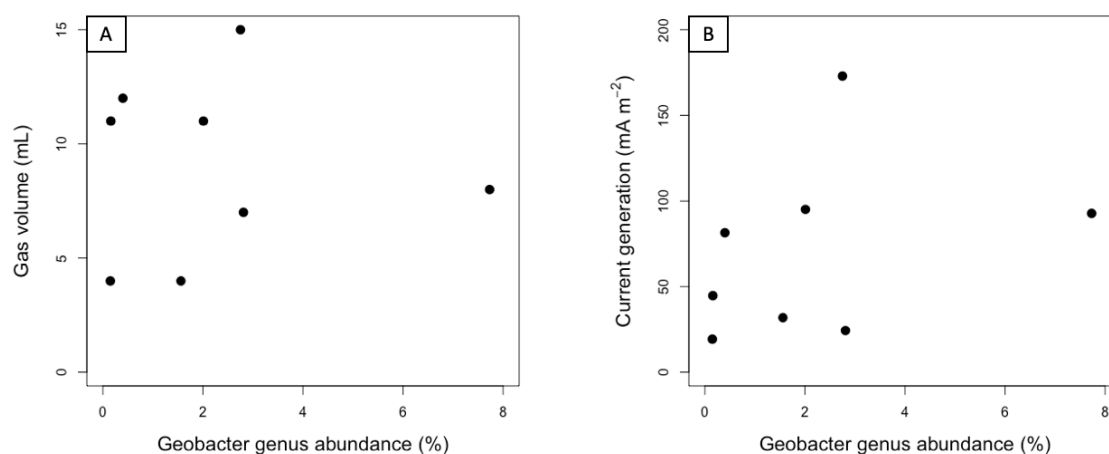


Figure 3-10: *Geobacter* abundance against gas production (A) and current generation (B)

Shewanella genus are documented as being manganese (IV) reducers in oxygen limiting environments, also being able to produce forms of the Mn (IV) depending on the conditions in which they are growing.¹²⁷ This genus was very low in abundance compared to the other exoelectrogenic genera identified in all MECs (Table 3-8). However, they were up to 2 orders of magnitude higher in the MECs that had manganese oxide coatings, suggesting that the presence of manganese (IV) was having a significant impact on their relative abundance. Based on finding in literature, it would seem that this difference is directly due to the presence of manganese (IV) oxide (based on their known interactions with Mn (IV)).¹²⁷

Sulfate reducing bacteria (SRB) genera were found on all anodes in the MECs but are in higher abundance on the plain M100 compared to the manganese (IV) coated materials. The M300 MnOx also had a relatively low abundance of SRB compared to the plain M100. SRB are obligate anaerobes that reduce sulfates to hydrogen sulphide, a dangerous gas that is toxic to humans and can corrode steel and concrete.^{128,129} In MECs, SRB can consume hydrogen as part of their metabolic pathway, reducing the overall performance of an MEC, particularly if SRB are able to colonise the cathode (the site of hydrogen evolution).⁶⁷ It has been reported that

manganese (IV) oxide is not reduced by SRB so it is possible that the presence of manganese (IV) oxide on the anodes was dissuading the proliferation of the SRB in the biofilms.¹³⁰ As higher quantities of gas were produced by the MECs that had manganese (IV) oxide coatings and these MECs also had lower SRB abundances, there is a strong indication that the reduction of SRB is due to the manganese (IV) oxide, which has improved performance. Furthermore, as SRB can cause many problems in other stages of the wastewater treatment industry (particularly in sewers)¹³¹ there could be value in using these kinds of materials further upstream in the wastewater treatment process, to reduce the proliferation of these taxa and reduce the damage they can cause to wastewater treatment assets, not to mention reduce odours and the risk to public health.

Arcobacter genus microorganisms are known manganese (IV) reducers and were found to be more prevalent on the manganese (IV) oxide coated materials compared to the plain M100 or the graphite felt (Table 3-8).¹³² *Arcobacter* can use manganese (IV) oxide as their terminal electron acceptor, explaining the higher abundances of this genera in the manganese (IV) coated MECs (2,4,7 and 8). *Arcobacter* is documented as having exoelectrogenic species (e.g. *Arcobacter butzleri*) so it's possible that their increased proliferation due to the manganese (IV) oxide has had a positive impact on performance, particularly regarding current generation.¹³³

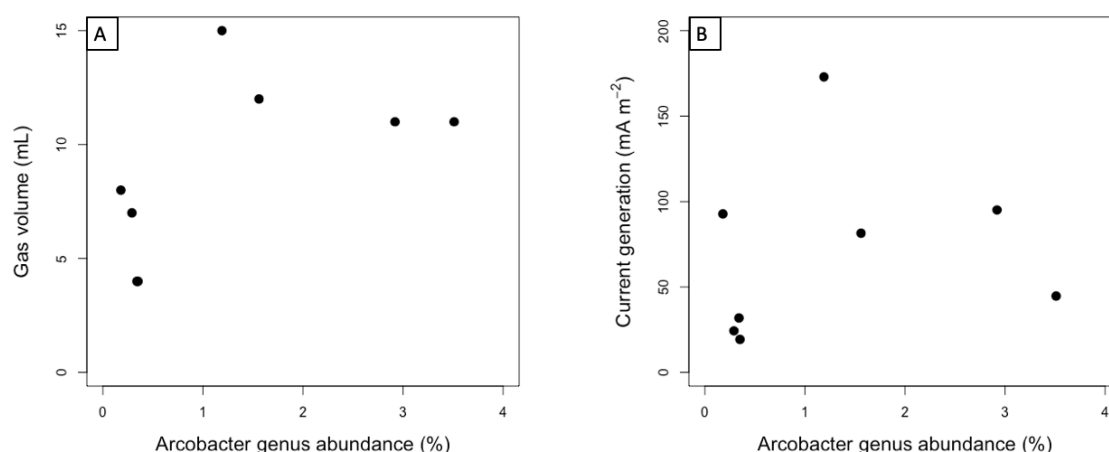


Figure 3-11: *Arcobacter* genus abundance against hydrogen production (A) and current generation (B)

However, similarly to the *Geobacter*, there is not a strict positive correlation between highest current or hydrogen gas production against higher abundances of *Arcobacter*

(Figure 3-11). This supports the concept that no single exoelectrogenic microbial taxa is preferable, but instead, the syntropy between the different species plays an important role.

All of the biofilms had very diverse (and equally diverse) communities (Table 3-9), both supported by strong values for Simpsons index of diversity (1 = highest diversity) and Shannon's diversity index (higher is more diverse). Therefore, the different materials did not have a significant impact on the overall diversity of the biofilms and any differences in performance will not have been brought about by overall diversity differences, as there were none.

Table 3-9: Simpsons and Shannon's diversity indices

Indices	MEC 1	MEC 2	MEC 3	MEC 4	MEC 5	MEC 6	MEC 7	MEC 8
Simpsons index of Diversity	0.997	0.997	0.998	0.997	0.995	0.996	0.996	0.997
Shannons Diversity	1.500	1.548	1.610	1.569	1.447	1.495	1.468	1.678

The manganese (IV) oxide coated materials have a lower abundance of *Geobacter* genus than the non-coated materials, but they also have higher abundances of the *Arcobacter* and *Shewanella*, so the overall diversity of exoelectrogens could be higher on these anode materials was having a positive impact on performance.⁴⁶ The performances of the systems will also have been enhanced by the reduced abundances of SRB genera which can be detrimental to the performance of an MEC.

3.4 What does this mean for the successful deployment of MECs?

The current generation for all systems was lower than expected (when compared to normalised literature values of similarly sized MECs).^{121,134} Despite this, given that the SGL graphite felts have been used for pilot and smaller lab-scale systems, the lower currents reported here are more likely to be due to the setup and higher resistances of the system.⁶⁷ Furthermore, lab-scale systems tend to be fed with a higher strength and less complex feed (sodium acetate dosed media as a synthetic wastewater where the concentration of the sodium acetate far exceeds the concentration of the organic compounds found in secondary wastewater).^{59,135,136} This means that it is fair to make comparisons between these systems and infer that the recycled carbon fibre

electrodes can function comparably to the graphite felts, particularly with the coatings of manganese (IV) oxide. Particular emphasis should be placed on the current generations that responded to increases to the organic loading rate, as the recycled carbon fibre anodes (in particular the M300 MnOx) were able to sustain higher currents after the higher dosage of COD, in some cases higher than the currents generated by the graphite felt. The M300 MnOx materials have outperformed the graphite felt as anode materials and have done so at a significantly reduced cost. This is encouraging and warrants further investigation in more realistic wastewater treatment conditions and ideally, at a larger scale.

Other than for MEC anodes, the knowledge that the presence of manganese (IV) oxide has reduced the abundance of SRB could have other applications outside of MEC technology, giving rise to the potential of architectural innovation. This would need to be confirmed with the materials being used in isolation of a voltage application, but this could have value for wastewater treatment companies to reduce concrete damage from hydrogen sulphide and reducing the risk of harm to the public, as well as any unpleasant odours.

3.5 Summary

The main focus of this stage of the project was to ascertain whether the recycled carbon fibre anodes would work in any capacity as anodes in MECs, compared to a known material that has worked successfully in MECs. To that end, the recycled carbon fibre anodes (both with MnOx and plain) have worked as MEC anodes. The overall difference between the systems in terms of performance was not very large, as all MECs were able to achieve total average removal rates between 83.23-84.62%. However, when the flow rate was increased, more significant differences in wastewater treatment efficacy were observed (8.3% between the best and worse materials, MnOx coated M300 and plain M100 respectively). It was during the increased organic loading rates that increased hydrogen gas production was also observed, but due to malfunctioning equipment and problems with gas collections, differences between the MECs were not significant.

The potential for hydrogen production estimated from the COD removal was over 99% greater when compared to the measured recovered hydrogen. The lack of hydrogen

recovery in all systems has contributed to the poor energy recovery and coulombic efficiency calculations as well. The low hydrogen recovery was likely caused by four main factors: Leakages, use of the Entek membrane, collection method and the depletion of the NaCl catholyte. As the conditions applied to all cells were all identical, the conclusion is supported that the hydrogen production from the cells with the manganese (IV) oxide coated M300 anode is higher than with the graphite felt benchmark material. Cell 8 (M100 MnOx anode) also produced hydrogen gas in the first round of sampling, where both the graphite materials (Cells 1 and 2) and uncoated M100 materials (5 and 6) failed to produce any detectable hydrogen gas (it was unfortunate that the confirmation of the differences in recoveries of gas from the other cells could not be achieved due to the faults encountered mid testing of the gas by gas chromatography during the second round of testing). The statistical analysis of variance using Anova, demonstrated that the differences in performance (COD removal and gas production) was not significantly different between MECs or the difference anode materials in the conditions used in the experiments described.

All of the materials sustained biofilms, but it was clear that the plain M100 material was lacking in coverage, compared to the other three materials. The graphite materials compared to the recycled carbon fibre materials coated in manganese (IV) oxide (both M100 and M300) had comparable levels of biofilm covered (based on the SEM images). The explanation for the differences in current generation and hydrogen production could be due to the impact that the manganese (IV) oxide has had on the abundance of certain genera of microorganisms. The highest abundance of *Geobacter* was detected on the graphite and uncoated M100 anodes, normally insinuating lower performance.⁴⁶ Instead, other exoelectrogenic bacteria were detected in higher abundances on the manganese (IV) oxide coated anodes, including *Arcobacter* and *Shewanella* genera. The manganese (IV) oxide has also reduced the presence of sulfate reducing bacteria (SRB) – where normally lower abundances of SRB correlated with improved performance, due to the reduction of hydrogen consumption by the SRB.

It is possible, that there are indeed not significant differences between the materials in terms of performance, with particular reference to the graphite felt and the three recycled carbon fibre-based anodes. Though an improvement in performance over the

graphite would be desired, it would not be essential to consider larger pilot-scale deployment of an industrially scaled MEC. What is significant, is the difference in cost, between the graphite felt and the recycled carbon fibre materials (£88 m⁻² for the graphite felt tested here and £1.84 or £5.52 for the plain M100 and plain M300 – costs of manganese were not calculated at this stage) – which is the main barrier to deploying the technology at scale.⁷⁹ Acceptable performances were achieved by the *Cotterill et al.* pilot using the graphite felt,⁶⁷ with major savings to the operating costs of a wastewater treatment plant possible, where the limiting factor halting deployment was the capital cost of the system (likewise with the *Heidrich et al* pilot).⁷³ If comparable performances can be achieved with the waste derived carbon fibre anodes, a major step to the deployment of an MEC at an industrial scale will have been made. The results generated from this stage of the project required reaffirming at a larger scale, as this will give a clear indication of whether the functional recycle carbon fibre materials are suitable for a more realistic MEC architecture. Therefore, a small-scale pilot test was required.

4 Putting innovation to the test: scale up with mini pilots

4.1 Demonstrating innovation by successfully running a pilot reactor

Innovation for an MEC would be defined as the successful deployment of the technology for an industrial application,⁷⁷ and for the case of wastewater treatment, this would require that deployment at a much larger scale than any other previous examples.^{67,76,83,137} Therefore, there was a need to show that these systems can work at larger-scale but with lower costs.⁷⁹

Originally, the use of platinum on for cathode (via doping) was a major barrier to deployment, as the platinum would be corroded over time and is a very expensive material.^{55,138} However, the use of stainless steel or nickel cathodes (which have demonstrated comparable hydrogen productions) means that this component of the MEC is no longer the cost limiting factor.^{55,139} The use of a proton exchange membrane (PEM) is another very costly component of the MEC,¹⁴⁰ but examples lacking a membrane or using inexpensive non-selective lead-ion battery separators (Entek) have demonstrated product recovery and the capacity of MECs to provide wastewater treatment.^{76,119} Even with the use of inexpensive cathode and membrane components, the MEC is still too expensive to deploy at larger-scales and this is caused by the price of virgin graphite or carbon felts. This results in the anode (and its current collector) comprising up to 90% of the total cost of an MEC.⁷⁹ Thanks to the sheer amount of cost saving that has been achieved by the use of the inexpensive cathode and membrane, the anode is now the cost limiting component that requires reduction.

The carbon felts used in the *Heidrich* pilot (Olmec) worked well as anodes, but had a high cost (£285.9 m⁻²). A large cost reduction was achieved in the *Cotterill* pilot, where the use of graphite felt (SGL Carbon) reduced the anode cost to £88 m⁻² but even this cost saving would not be enough to make the MEC cost-competitive (from a capital cost perspective) compared to standard wastewater treatment assets such as activated sludge plants (ASP).⁶⁷ Assuming the performance in the *Heidrich* pilot is maintained, a 90% reduction in the combined cost of the anode and the current collector would be required to make the MEC cost-competitive with an ASP.⁷⁹

The recycled carbon fibre anodes do offer the potential to drastically lower the cost as they are over 98% and 93% less expensive than the Olmec and SGL materials. It was confirmed that the recycled carbon fibre anodes were able to maintain a biofilm and work to treat wastewater, but the hydrogen recoveries (and therefore the efficiencies) were very low (N.B. this was for all of the MECs, including those that used SGL graphite felt which has been confirmed as a functional anode for hydrogen gas production in an MEC).⁶⁷ The experiments in Chapter 3 were also at a very small-scale (compared to other pilot studies) and with non-optimised architectures for product recovery in an MEC (e.g. large electrode spacing between the anode/cathode and high chance of leakage from the reactor chambers)^{44,141} that would not be appropriate for the requirements of a wastewater treatment asset. Therefore it is clear that the nature of the architectures and operation will require alteration to attain improved confirmation as to whether these recycled carbon fibre anodes have the potential to deliver on innovation for MECs.

To confirm whether there are significant differences in performance between the recycled carbon fibre materials and the graphite felt, a second round of tests was required. As it is also the aim of this project to confirm whether larger-scale systems are financially viable, larger-scale MECs were desired. It was decided that the next phase of the project should be conducted with larger dimension MECs and at a wastewater treatment plant..

4.2 Pilot reactor setup and operation

4.2.1 Reactor architecture and construction

Similar designs to the *Heidrich* and *Cotterill et al* pilots were used, as they were simple to design and manufacture (Figure 4-1 and Figure 4-2).^{67,73} Furthermore, they allowed for a rapid method to compare the different anode materials, which have been identified as the key barrier to large scale MEC application.

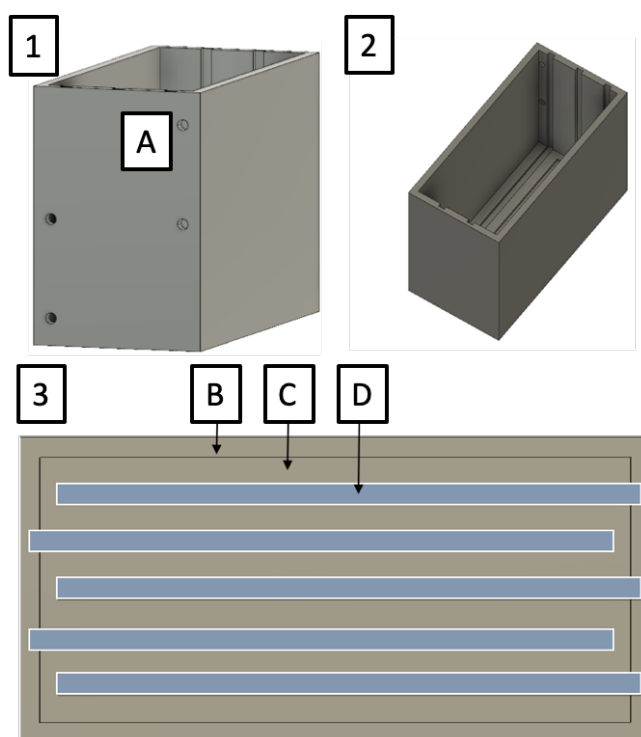


Figure 4-1: Reactor CAD design

1) Side view of reactor chamber with input and output holes (A). 2) Raised side view of the reactor chambers showing the grooves to which the module cassettes connect to. 3) Top view of the reactor with the walls (B), anode area (C) and module slots (D).

The MECs had a volume larger than 10 litres, but taking into account the headspace and space taken up by the components of the modules, the working volume was 8 L. Table 4-1 shows the important dimensions of the mini-pilot MECs.

Table 4-1: Dimensions of the MEC reactors

Total anodic area (m ²)	Total cathodic area (m ²)	Working Volume (L)	Anodic surface area to volume ratio (m ² m ⁻³)	Cathodic surface area to volume ratio (m ² m ⁻³)
0.61	0.24	8.03	75.57	30.26

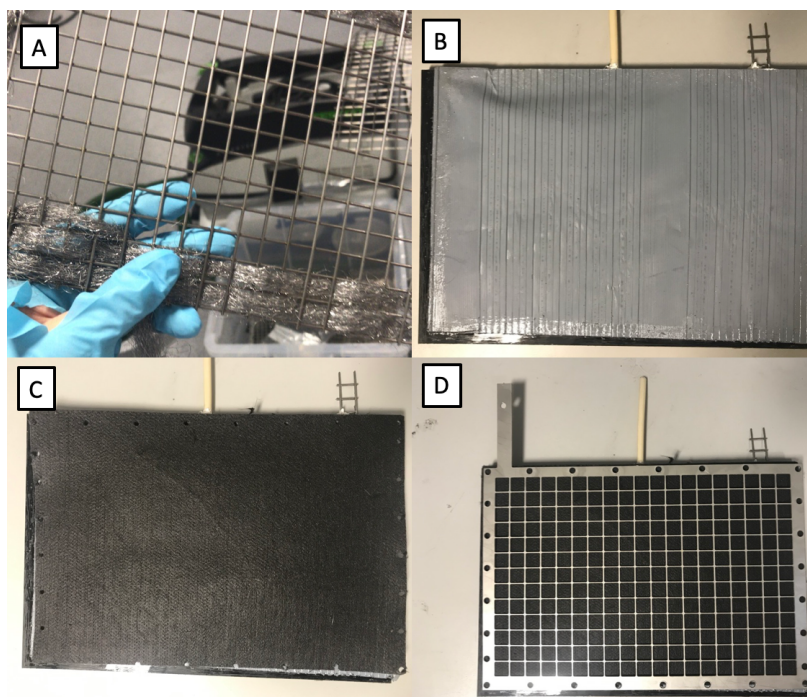


Figure 4-2: Module assembly

The modules were assembled as follows: The cathode was constructed (A) and placed in the module with the tab protruding through the top of the cassette. This was then sealed in place on both sides with the Entek separator using glue (B). The anode material of choice was then placed on both sides of the cassette (C). The current collector was then to fixed both sides of the cassette and bolted in place (D).

The anode materials tested and their respective MEC number is detailed in Table 4-2.

Table 4-2: MEC codes and anode material details

MEC code	MEC 1	MEC 2	MEC 3	MEC 4
Anode material Description	M-Carbiso of 300 g m ⁻² (M300) coated with manganese (IV) oxide	M-Carbiso of 100 g m ⁻² (M100) coated with manganese (IV) oxide	M-Carbiso of 300 g m ⁻² (M300)	SGL GFD 4.6 felt
Anode material code	M300 MnOx	M100 MnOx	M300 Plain	SGL 4.6

The MECs were then placed on a steel bench close to the pumps and wastewater reservoir (Figure 4-3).

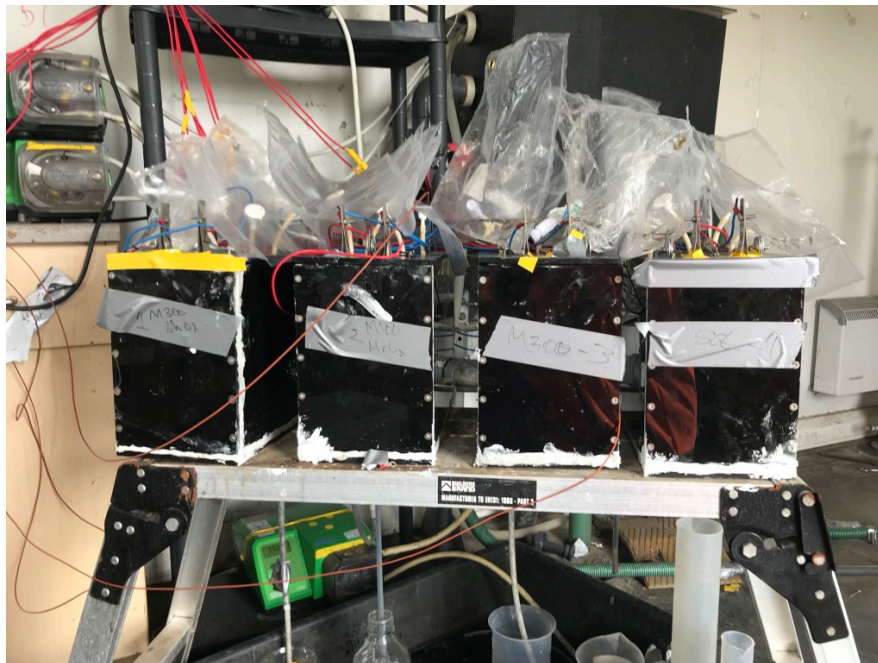


Figure 4-3: Photo of the four MECs in the Portakabin

4.2.2 Operation

The MECs were fed with real wastewater at a constant HRT of 5 hours. The wastewater was primary effluent (before treatment in an activated sludge pool). There was no ferric chloride dosing in the water used in this experiment. Pumps were used to move the water from the separating channels at the wastewater treatment plant to a reservoir in the portacabin (where the pilots were operated). Four peristaltic pumps (520S, Watson Marlowe) were used to feed the MECs (Figure 4-4).

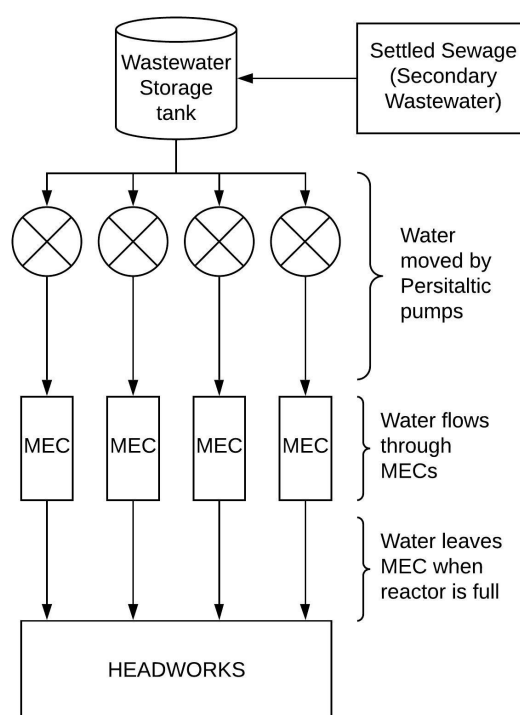


Figure 4-4: Process flow schematic for the Pilot MECs

A power supply (Tenma) was used to power two MECs at the same time (which power supply had two sets of channels). A voltage supply of 1 V was used.

4.2.3 Parameters measured

Gas volumes were measured using a 100 mL borosilicate glass syringe (error of 4%) and the concentration of hydrogen gas was determined using a GC (Micro GC, Agilent), using the same calibration curve used for the hydrogen gas analysis in Chapter 3.

Wastewater treatment was monitored by using HACH COD and nutrient cuvettes: 0-1000 mg L⁻¹ COD (LCI400), COD 15-150 mg L⁻¹ (LCK314), phosphates (TNT 845), nitrates (LCK 339), nitrites (LCK341), sulfates (LCK153) and sulfides (LCK653). Total suspended solids (TSS) were also measured by filtering influent/effluent through glass fibre filters using a pump and then using an oven to evaporate the moisture (allowing for the weighing of the solids). TSS can cause harm to rivers if released and require a minimum of a 50% reduction in concentration before effluent is released to the environment.¹⁴²

Current was measured using a data logger (Pico-logger, Picotech) to measure the voltage drop across a known sense resistor, which was soldered into the wires that supplied voltage from the power supply to the cathodes of the MECs. Originally, a 1-ohm resistor was used, but this was too high for the MECs, so this was changed after 10 days to a 0.1-ohm resistor. A schematic of the setup is shown in Figure 4-5.

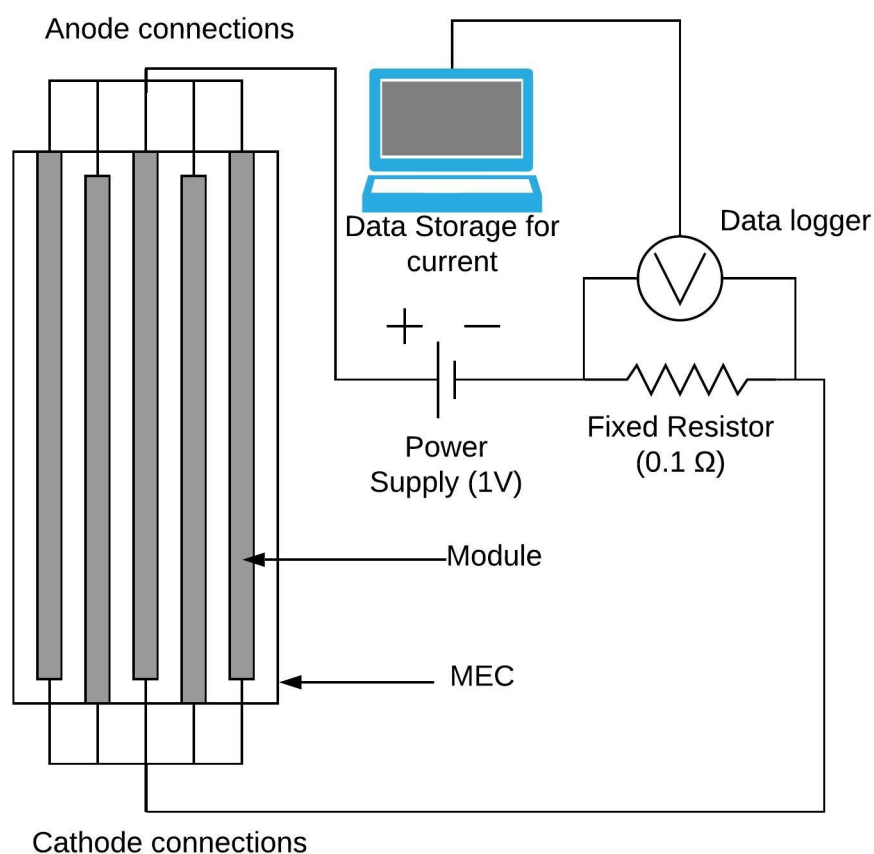


Figure 4-5: Electrical connection schematic for each MEC

From day 36, temperature was recorded with a Picotech temperature data logger with miniature 0.25 mm diameter mineral insulated thermocouples with a pot seal (TC Direct). One was dipped into the reservoir of wastewater and then one into each MEC reactor. pH was spot-checked using a HACH-Lange multi-meter (HQ40D) and a PHC20101 pH probe (HACH-Lange).

4.2.4 Microbiology

3 replicates from each anode (a total of 60 samples from each MEC) were acquired and frozen at -80°C in preparation for DNA extraction using the techniques described in Chapter 3 (soil DNA FASTprep extraction kit (MP Biomedical)). SEM samples were also prepared using the same techniques described in Chapter 3 in this Innovation Report.

4.3 Pilot reactor results

After 90 days of operation, the MECs were decommissioned and data collected up to this point was used to assess the performance. Comparative T-tests and one way Anova tests were used to determine whether the differences in performance was significant. Therefore, the hypotheses were:

H_0 = there will be no difference in performance* between the MECs that are using different anode materials.

H_1 = there will be a difference in the performance* of the MECs which will be dependent on the anode material used.

*Performance = hydrogen gas production, wastewater treatment performance and current density.

4.3.1 Wastewater treatment performance

Total COD removal rates

The average chemical oxygen demand (COD) removal rates from the MECs were not high enough to meet the urban wastewater treatment directive limit of 125 mg L⁻¹ or the 75% removal amount (Table 4-3).¹⁴

Table 4-3: Percentage removal of COD from the MECs

COD removal value	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode material code</i>	M300 MnOx	M100 MnOx	M300 Plain	SGL 4.6
<i>Total average %</i>	24.55	24.63	27.40	13.05
<i>Average from onset of gas %</i>	27.90	N/A*	31.42	15.37
<i>Peak %</i>	43.53	49.29	51.46	33.89

*MEC 2 has N/A-value due to the lack of gas production

The best performing MEC in this regard was MEC 3 (27%), which used the uncoated M300 as an anode and the worst average was MEC 4, using the graphite felt anode (13%). MECs with HRTs of 5 hours have been capable of treating secondary wastewater to higher standards than those recorded in this Innovation Report using the same graphite felt (SGL, GFD 4.6) as an anode, suggesting that the architecture, size and other components of the MECs were not optimal for wastewater treatment performance.⁶⁷ However, when comparing the anodes in this experiment, it is clear that the recycled carbon fibre anodes have a performance advantage over the graphite felt.

However, the MECs did show continual improvement in the % of COD removal from the start point of the trial, until day 56 (Figure 4-6). The highest (COD) removal rate (both in terms of % and mg COD removed) was for MEC 3 at day 56, achieving a 51% removal (317 mg COD removed from 616 mg). MEC 3 achieved this using the least expensive material (Plain M300), with MECs 2 and 1 close behind, in terms of removal (49 and 43% respectively). The progressive increase in the % of COD removal suggests that the biofilms on the anodes of the MECs were growing which was resulting in an improvement to wastewater treatment, attributed to the increased oxidation of organic matter by the microorganisms (this is supported by the increases in current, which are discussed in Section 4.3.6).¹¹⁹

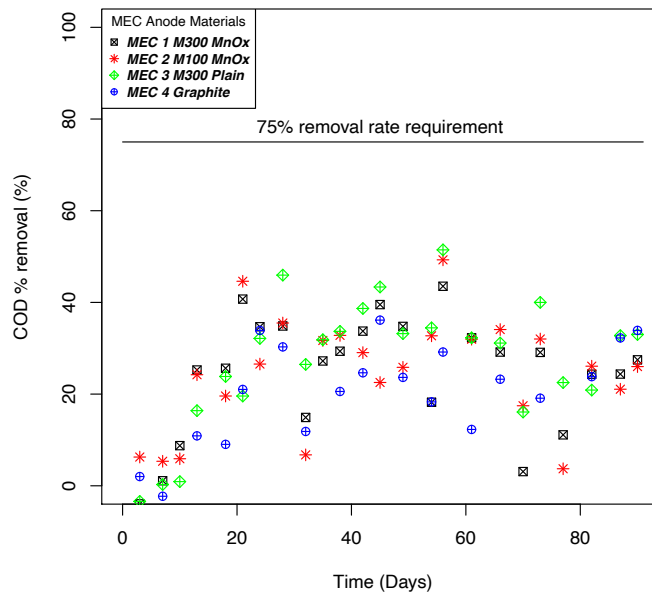


Figure 4-6: COD % removal over time

Following day 56, unseasonably cooler temperatures and heavy rainfall persisted for over a week (days 63-70, to the point where “storm conditions” were declared at the wastewater treatment plant) resulted in a drop in COD removal %. The lower ambient temperatures of the input wastewater were brought about by the increased rainfall, but this appeared to have no impact on the internal temperatures of the MECs. Lower temperatures can negatively impact the microbiological activity of MECs reducing the rate of substrate oxidation,¹⁴³ as well as the lower concentration of substrate may have resulted in community death reducing the quantity microorganisms on the anodes.^{82,116} Colder temperatures reducing COD removal has been reported in the literature.¹⁴⁴ Following the cooler period, the % removal did begin to increase again (days 78-90). The worst performing MEC in terms of peak COD % removal was MEC 4 with 33% removal (graphite felt). Overall, the average % COD removal was better for all of the recycled carbon fibre anode materials compared to the graphite anode MEC (Table 4-3). An explanation for this could be an improved fibre spacing between the carbon fibres in the recycled carbon fibre mats, relative to the graphite felt. The graphite felt was a lot more dense and appeared to be more compressed by the current collectors whereas the recycled carbon fibre anodes had less mass per unit area resulting in less compression, which could have enabled better coverage by

biofilm, meaning an improved surface area to volume ratio which is beneficial to MEC performance.^{115,145}

MEC 3 had the best quality average effluent (total and after the onset of gas production) as well as removal, with MEC 4 being the worst (Table 4-4). The average removal for MEC 3 was 107 mg L⁻¹, almost double MEC 4 (57 mg L⁻¹).

Table 4-4: COD removals and concentrations in effluents

Measurement	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode material code</i>	M300 MnOx	M100 MnOx	M300 Plain	SGL 4.6
<i>Average output concentration (mg L⁻¹ as COD)</i>	278.67	280.63	261.30	299.04
<i>Average removal (mg L⁻¹ as COD)</i>	99.08	96.17	107.32	57.25
<i>Average removal from the onset of gas production (mg L⁻¹ as COD)</i>	111.70	N*	122.99	65.12
<i>Average output from the onset of gas production (mg L⁻¹ as COD)</i>	265.00	N*	250.01	279.54

*MEC 2 has N- value due to the lack of gas production

Figure 4-7 shows how there was little difference in COD removal performance between the different MECs that used different forms of the recycled carbon fibre anodes, as the black, red and green points are relatively well clustered up over one another. This indicates that the manganese (IV) oxide is having less impact (or arguably a negative impact) at these larger-scales compared to the wastewater treatment performance differences in the previous experiment and chapter (section 3.3.2). The method of voltage supply (applied voltage from a power supply instead of a fixed voltage on the anode) is having a different impact on the microbial community compared to the use of the potentiostat to power the MECs in Chapter 3. The increased resistance from the manganese (IV) oxide could be affecting the rate of COD oxidation.⁹⁴

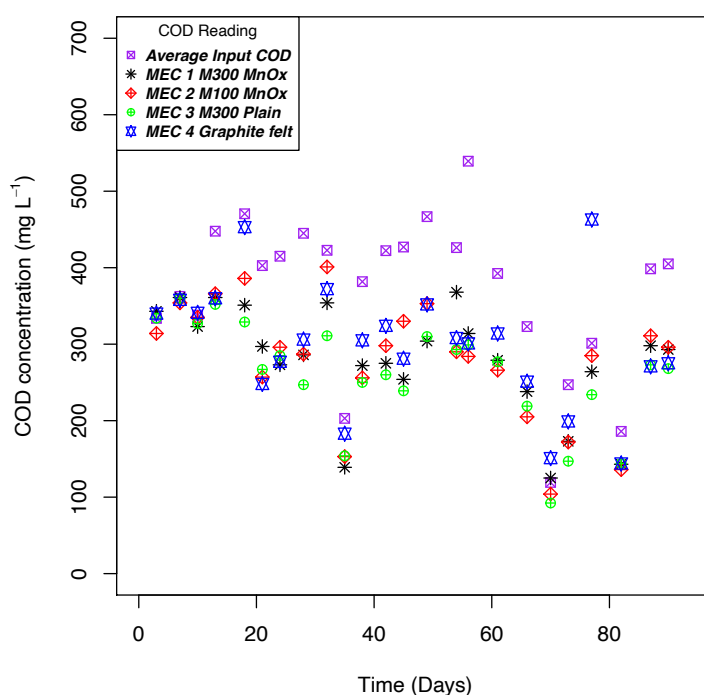


Figure 4-7: COD concentration from each MEC effluent compared to the average COD input.

MEC 4 has the most instances where the effluent had the highest COD concentration 11 times out of 24 readings (MEC 3 had one effluent that was worst by comparison - Table 4-5).

Table 4-5: Number of best and worst COD readings for the MECs

	MEC 1	MEC 2	MEC 3	MEC 4
Times Best	4	7	11	2
Times Worst	5	7	1	13

The T-test produced P-values which suggested the COD removal (in terms of mg L⁻¹) from MECs 1 and 3 were significantly better than MEC 4 (P-value ≤0.05). MEC 2 had a P-value of >0.05 meaning the performance difference in terms of COD removal was not significant and this is likely due to its smaller availability of surface area which has resulted in this microbial oxidation of organic compounds and therefore, worse wastewater treatment. Percentage COD removal did have significant differences, with all three MECs producing calculated P-values of; ≤0.05 (Table 8-4 in the appendix). When comparing the P value from the one way Anova tests, it supports the first T-test result; that the anode material did not have a significant impact on COD removal, as the P-value was 0.386 (Equation 4-1). Similarly, the one way Anova also indicates that the variance between the different removal rates for the different MECs is not significant, with a P-value of 0.281 (Equation 4-2).

Equation 4-1: COD concentration Anova - $F(3,92) = 1.024, p = 0.386$

Equation 4-2: COD removal Anova – $F(3,92) = 1.293, p = 0.281$

4.3.2 TSS Removal

A minimum removal of 50% of total suspended solids (TSS) is required for discharged effluents. All of the MECs achieved this but there were some significant differences in their TSS removals (Table 4-6). The reduction of the TSS would have been brought about by microbial oxidation of the solids (resulting in hydrolysis of the solids) at the site of the anodes, solid build-up on the fibres and settling of the solids in the reactors, which has been confirmed in a pilot study.⁶⁹ The design of the reactor is very important for reducing TSS in effluents. Different mass particles (i.e. the TSS) have a different settling times (i.e. the heavier the particle are the faster it settles), therefore the flow of wastewater, the length and width of the reactor will have to be designed to ensure that any wastewater it treats has the time to settle/be treated before it leaves the reactor.¹⁴⁶ This will need to be considered for any future MECs.

Table 4-6: TSS removal performances for MECs

	MEC 1*	MEC 2	MEC 3	MEC 4
<i>Anode material code</i>	M300 MnOx	M100 MnOx	M300 Plain	SGL 4.6
<i>Total removed (mg)</i>	975	1055	1530	985
<i>Average removal (mg)</i>	54.17	58.61	85.00	54.72
<i>Average percentage removal (%)</i>	56.18	61.47	88.24	57.94
<i>Peak percentage removal (%)</i>	90.00	88.89	100.00	84.62

*MEC 1 had a pump issue which introduced a high dose of sludge mid-operation (day 54).

In terms of percentage and mass removal of TSS, MEC 3 is again the best performing MEC, with MEC 1 being the worst (affected by pump issue on day 54 where highly concentrated sludge was pumped into the MEC). MEC 4 performed poorly compared to the MEC 3, moving 30% less suspended solids. As MEC 3 performed better than MEC 1 (and they both used the same material bar the introduction of manganese (IV) oxide) the difference in TSS removal between the graphite felt and the M300 recycled carbon fibre materials will not have been brought about by increased settling of solids on the anodes. If this was the case, then the TSS removal rates for MEC 1 and 3 would have been smaller and the TSS removal rates for MEC 1 and 4 would have been greater (they were almost the same - Table 4-6). This suggests that the microbial action of TSS removal was best on the plain M300 anode material in MEC 3, with the manganese (IV) oxide harming performance.

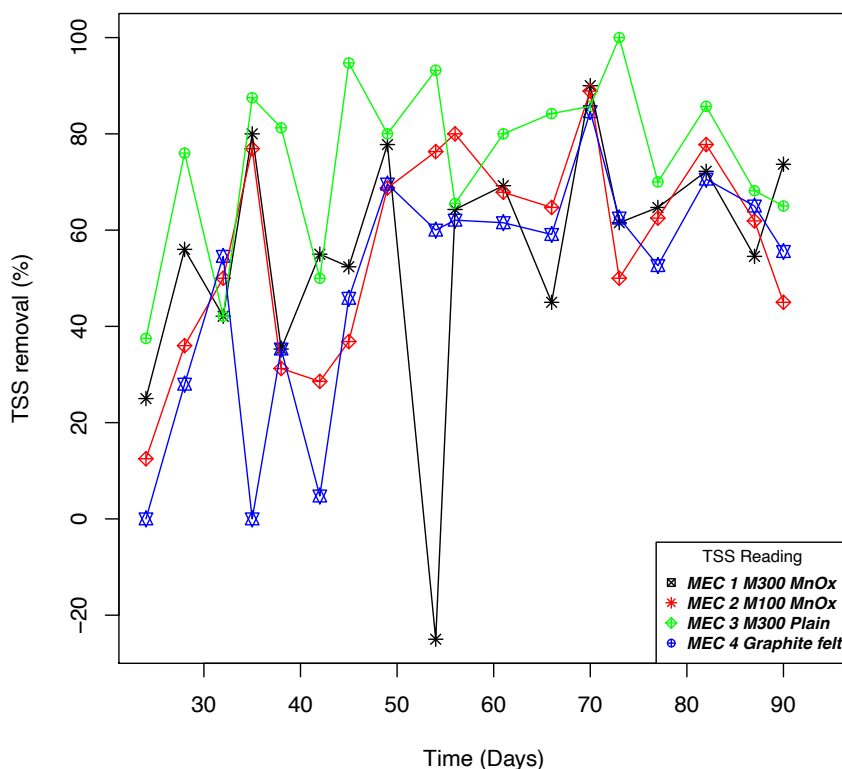


Figure 4-8: Percentage of TSS removed from effluents from MECs

Figure 4-8 demonstrates that MEC 3 had the lowest percentage of TSS remaining following treatment (the green points have the most instances where they have the highest TSS % removal). The single reading with a negative value (below 0% - day 54) for MEC 1 was the reading that suffered from a pump issue and expelled a high quantity of solids into the reactor.

Despite the largely improved removal of TSS removal by MEC 3 compared to MEC 4, the difference is not considered to be a significant improvement when using an R squared test ($P\text{-value} > 0.05$) and is the same for MECs 1 and 2. However, in terms of percentage removal of TSS from wastewater, MEC 3 does perform significantly better ($P\text{-value}$ of < 0.002 when a value of 0.05 would already considered significant - Table 8-4 in the appendix).

4.3.3 Nutrient Removal

Low nutrient removal was reported throughout but nitrite, sulfate and organic acid removal were consistently recorded (Table 4-7). Sulfide was relatively unchanged, with nitrate and phosphorous increasing. Nitrate increases were expected due to the

oxidation of nitrite to nitrate by *Nitrobacter* and *Nitrosomonas* genus, which although has been confirmed by 16S sequencing of anode samples from this trial, these genera of bacteria were identified in the MECs in Chapter 3 and are common taxa identified in wastewater treatment environments.¹⁴⁷

Table 4-7: Average nutrient removal from each MEC (negative values indicate an increase in concentration)

	Anode	Nitrate (mg L ⁻¹)	Nitrite (mg L ⁻¹)	Phosphorous (mg L ⁻¹)	Sulfide (mg L ⁻¹)	Sulfate (mg L ⁻¹)	Organic acids (mg L ⁻¹)
MEC 1	M300 MnOx	-0.40	0.20	-0.17	0.13	48.18	43.16
MEC 2	M100 MnOx	-0.51	0.21	-0.16	-0.08	54.72	41.51
MEC 3	M300 Plain	-0.87	0.24	-0.21	-0.08	57.01	39.02
MEC 4	SGL 4.6	-0.87	0.23	-0.20	-0.12	50.30	38.55

Sulfates would have been reduced to hydrogen sulfide by sulfate reducing bacteria (SRB), which like the *Nitrobacter* and *Nitrosomonas*, are common taxa in wastewater treatment environments,^{130,131} also explaining the sulphide increases in some of the MEC effluents (Table 4-7 and Table 4-8).

Table 4-8: Average percentage nutrient removal from each MEC (negative values indicate an increase in concentration)

	Anode	Nitrate %	Nitrite %	Phosphorous %	Sulfide %	Sulfate %	Organic acids %
MEC 1	M100 MnOx	-140.98	44.67	-7.12	0.93	58.70	21.89
MEC 2	M300 Plain	-158.79	45.05	-8.66	-5.56	60.05	19.05
MEC 3	SGL 4.6	-178.44	40.63	-10.96	-7.41	63.29	19.34
MEC 4	M300 MnOx	-156.48	38.54	-7.44	-13.32	62.86	17.13

The only MEC that had a decrease in sulfide (which was less than 1%) was MEC 1 – using the MnOx coated M300 anode. 16S sequencing demonstrated a reduced relative abundance of SRB presence of manganese (IV) oxide in the smaller MECs (Section 3.3.9), which could explain why MEC 1 has the lowest sulfate removal and best sulfide removal, as the SRB should be in lower abundances. Low phosphorous removal (and all nutrient removal for that matter) is common in MECs and was recorded in this trial, strengthening the need for further downstream treatment if MECs are to be deployed at scale, potentially a BES specifically tailored to phosphate removal.^{42,67}

4.3.4 pH changes

There was not a significant change in pH for any of the effluents when compared to the input pH for each MEC reactor (Table 4-9).

Table 4-9: pH changes for the MECs

MEC Code	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode material code</i>	M300 MnOx	M100 MnOx	M300 Plain	SGL 4.6
<i>Average pH in</i>	7.63	7.65	7.68	7.69
<i>Average pH out</i>	7.72	7.79	7.67	7.74
<i>Spread</i>	7.65 ± 0.44	7.78 ± 0.51	7.69 ± 0.27	7.63 ± 0.42
<i>Average pH change</i>	-0.09	-0.14	0.01	0.05
<i>Minimum pH out</i>	7.21	7.27	7.42	7.21
<i>Peak pH out</i>	8.08	8.28	7.96	8.05
<i>Range</i>	0.87	1.01	0.54	0.84
<i>Minimum pH in</i>	7.21	7.27	7.42	7.37
<i>Maximum pH in</i>	7.94	7.87	7.91	7.89

The variation in pH of the effluents from the same MEC was relatively low, with only MEC 2 showing a pH range of over 1 (7.78 ± 0.51). MEC 3 had the narrowest range; 0.54 (7.69 ± 0.27). The difference in the average pH change was small for all MECs. However, the cumulative pH changes for MECs 1, 2 and 4 were all negative, with MEC 3 being positive. The pH ranges were well within the 6.5-8.5 range where most microorganisms (specifically those in wastewater treatment plants) thrive.¹⁴⁸ The lack of variability in pH is promising as maintaining the anodic pH will be beneficial to the performance of the MECs, although any future pilots of this size should make efforts to monitor the pH of the catholyte to determine the difference between the two environments and ensure that the higher concentration of H⁺ ions is higher in the cathode chamber, to stimulate the evolution of H₂.¹⁴⁴

4.3.5 Hydrogen gas production

Start-up

Within a relatively short time, gas was produced in measurable quantities from MEC 3 (used recycled plain carbon fibre as the anode – ELG M300) – after 13 days of

operation. The days on which different modules began producing gas is detailed in Table 4-10.

Table 4-10: Initial gas production detection for each module

			Module				
		Anode material	1	2	3	4	5
MEC	1	M300 MnOx	87	93*	N	90	18
	2	M100 MnOx	N	N	N	N	N
	3	M300 Plain	13	77	13	28	38
	4	SGL 4.6	42	56	87	38	N

*Gas was collected and measured in the GC on the final day, but the GC suffered a fault post-measurement – gas volumes from day 93 are not included in the subsequent performance analysis but the fact that hydrogen gas was detected is still mentioned here.

MEC 1, which used anodes made from M300 coated with Mn (IV) oxide, looked to be very promising, with its 5th module starting up on the 18th day with confirmed hydrogen gas. This module continued to produce high purity hydrogen until the end of the trial. However, all of the other modules failed to produce any significant quantities of gas until the end of the experiment (modules 1, 2 and 4 specifically) with module 3 failing to produce any gas. MEC 2 used the same materials as MEC 1, just with a thinner electrode (M100 material instead of M300 – therefore 100 g m⁻² instead of 300 g m⁻²). The MEC never entered into a period of gas production. The least expensive and most sustainable anode material (plain ELG M300) used in MEC 3 was the first to ‘start-up’ in terms of gas production and was also the first and only MEC that had all of its modules producing hydrogen gas. MEC 4 had the longest start-up period (38 days until gas was produced) but was able to produce gas from 4 different modules.

Faster start-up times are desired for MECs so that product is recovered as quickly as possible to cover the costs of running the technology, but also to initiate wastewater treatment performance. The plain M300 had the combination of lower resistance (relative to the MnOx coated M300/M100) and larger surface area (relative to the SGL due to the lack of compression by the current collector) are the two most likely causes of the faster start-up time.⁹⁴ The improvement over the graphite felt is particularly promising given the greatly reduced cost the M300 has over the graphite felt.

Hydrogen Gas Volume

The concentrations of hydrogen gas produced by the top two best performing MECs (MEC 1 and 3) had relatively high average hydrogen gas concentrations. The variation for MEC 3 was higher than that of MEC 1, as it had more modules that produced gas which went through periods of high and low performance. MEC 4 had a comparatively low hydrogen gas concentration; only 44% compared to 87% for MEC 1 and 78% for MEC 3 (Table 4-11).

Table 4-11: Hydrogen gas concentrations

	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode material code</i>	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
<i>Average %</i>	87.94	0.00	78.12	44.34
<i>St dev %</i>	10.52	0.00	20.28	21.06
<i>Peak %</i>	100.00	0.00	100.00	80.30
<i>Min %</i>	54.09	0.00	17.98	10.61
<i>Moles of hydrogen (M)</i>	0.50	0.00	1.67	0.10

The total volume of hydrogen gas produced differed greatly between the different reactors, where both MEC 1 and 3 produced significantly more hydrogen gas than MEC 4 (Table 4-12).

Table 4-12: Hydrogen produced from start-up; actual and normalised

MEC	Anode material code	Total volume of H ₂ (L 77 d ⁻¹)	Average daily volume of H ₂ (L d ⁻¹)	Normalized volume of H ₂ to 1 m ³ reactor (L 77 d ⁻¹)	Normalized daily volume of H ₂ to 1 m ³ reactor (L d ⁻¹)
1	M300 MnOx	12.21	0.16	1526.52	19.82
2	M100 MnOx	0.00	0.00	0.00	0.00
3	M300 Plain	41.13	0.53	5141.19	66.77
4	Graphite felt	2.25	0.03	281.05	3.65

Using a T-test, the difference in the hydrogen gas produced by MECs 1 and 3 was determined as being statistically significant (both with a P-value <0.001), indicating a high degree of confidence in the performance improvement of the recycled carbon fibre materials (both plain and coated with manganese (IV) oxide). The difference in the total amount of H₂ produced is visually very evident in Figure 4-9.

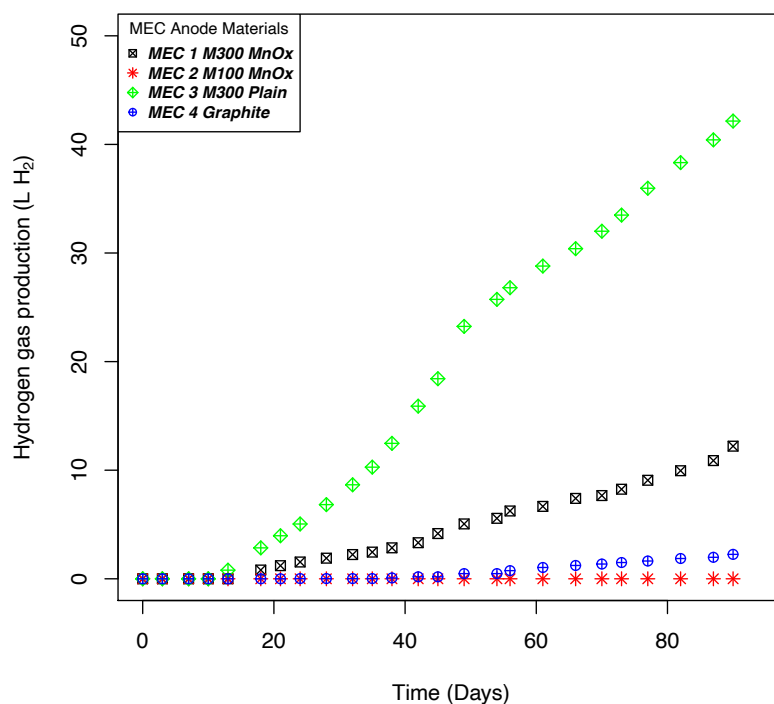


Figure 4-9: Cumulative gas production by each MEC over time

Figure 4-9 demonstrates the large improvement of hydrogen gas production that MEC 3 had over MEC 4 but also MEC 1. The rate of hydrogen gas production between day 40 and 50 also appeared highest for MEC 3, with a slowdown from day 50. The one way Anova test also supported the results of the T test that there was a significant difference in hydrogen gas production brought about by the different anode materials (Equation 4-3).

Equation 4-3: Hydrogen gas Anova $F(3,96) = 44.39, p = <0.001$

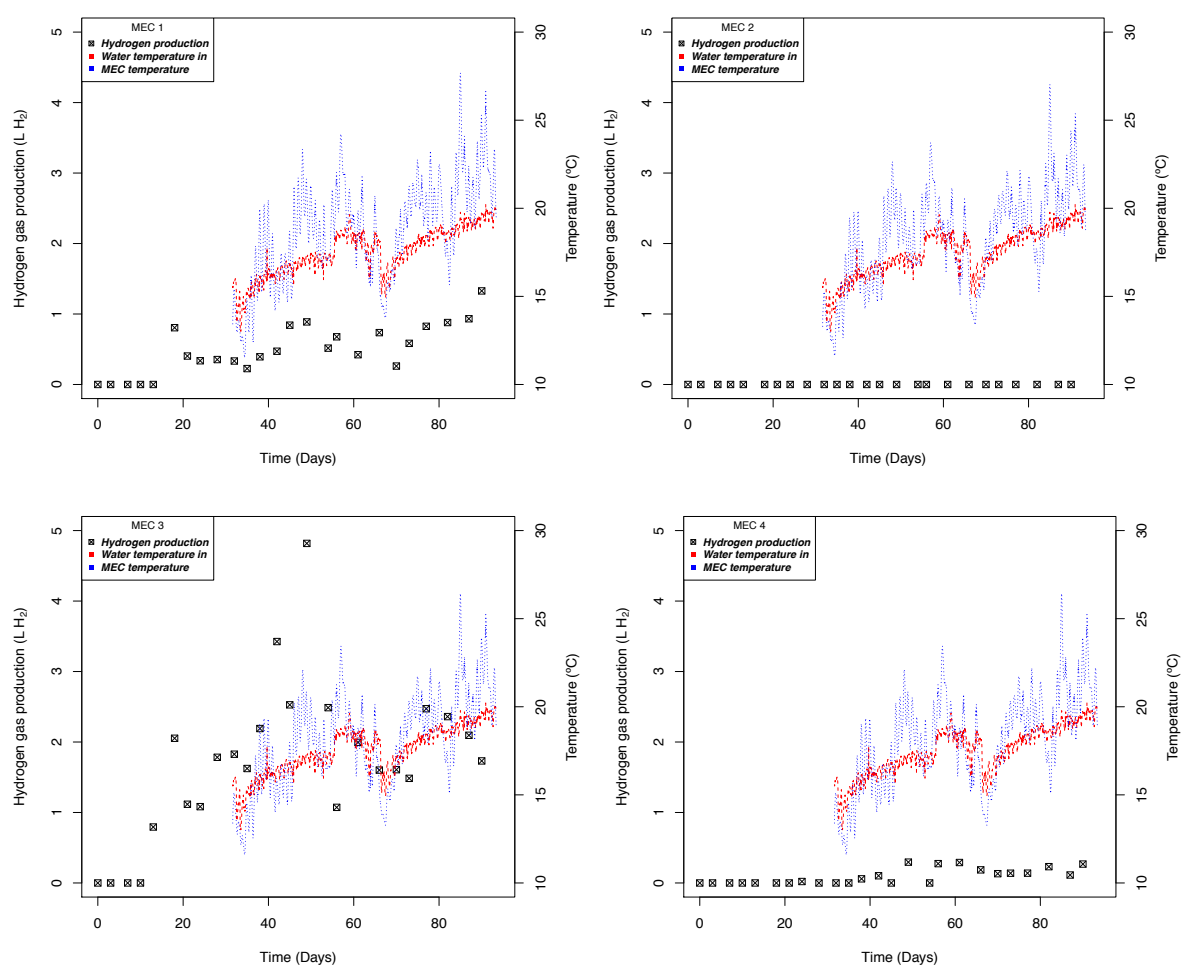


Figure 4-10: Hydrogen produced over time in relation to the temperature from each MEC (internal MEC and of the wastewater before treatment)

Temperature is reported to have a positive impact on hydrogen production from MECs, similar to its impact on COD removal (discussed in section 4.3.1).¹⁴³ MEC 1 had a strong positive correlation (Pearson values for all variables are listed in section 8.2.3 in the appendix) between hydrogen production ($R=0.91$), which is visible in Figure 4-10 – MEC 1, where increases and decreases in hydrogen production mimic the changing

internal MEC and wastewater temperatures. MEC 2 produced no hydrogen so there was no correlation. Though there will have been multiple factors that can be linked to the production of hydrogen for MEC 1, it is suggested that this MEC was temperature dependent. The increase in hydrogen production in the final days of the experiment was due to modules 1, 2 and 4 starting up which did coincide with some spikes in temperature. The increased resistance of the electrodes due to the manganese (IV) oxide may be the reason for the need for higher temperatures for MEC 1.

MEC 3 had a very low (arguably non-existent) positive correlation between temperature H_2 production. This was due to MEC 3's ability to continue producing hydrogen gas during cooler periods, but also because the rate of H_2 production did not continue to increase with increasing temperature (post day 49, before the storm conditions from day 63-70). As the temperatures reached a maximum of 25°C , the biofilms would not have been suffering from death from heat shock (30°C has been reported as an optimum temperature for BES performance).¹⁴³ Following day 49, the overall production of gas fell significantly for all MECs, dropping by 47% in MEC 3, before the storm conditions, so the reductions in performance are likely not linked to temperature. As the catholyte was not replaced at any time, it's possible that the NaCl solution was diluted and required replacement. Also, as the anodes used MEC 3 were lacking in manganese (IV) oxide there may have been a greater abundance of sulfate reducers which would have reduced the recovery of hydrogen, which the nutrient outputs with regards to sulfide and sulfate do support (discussed previously in section 4.3.3).⁶⁷

The overall gas production in MEC 4 was very low compared to MECs 1 and 3. Temperature increases appear to have stimulated increases in gas production, which is supported by an R-Value of 0.83. The lower resistivity of the graphite compared to the recycled carbon fibre electrodes would be expected to result in better performance,^{117,141} but this assumes that the nature of the porosity and spacing between fibres is the same between the graphite and recycled carbon fibres. It is very unlikely that this is the case with the graphite felt used in MEC 4 and the recycled carbon fibre anodes used in MECs 1-3, supported by the higher density of the graphite (460 g m^{-2}) compared to the recycled carbon fibre materials (similar thickness but with $100\text{-}300\text{ g m}^{-2}$).

4.3.6 Current generation

The current generations changed over time, with the different MECs producing different responses to the uncontrolled variables of temperature and COD input. Following the changing of the 1-ohm resistor with a 0.1-ohm resistor (Day 10), MEC 1 and 3 produced constant increases of their current generation. MEC 2 and 4 appear to have produced constant decreases during the same period (Figure 4-11).

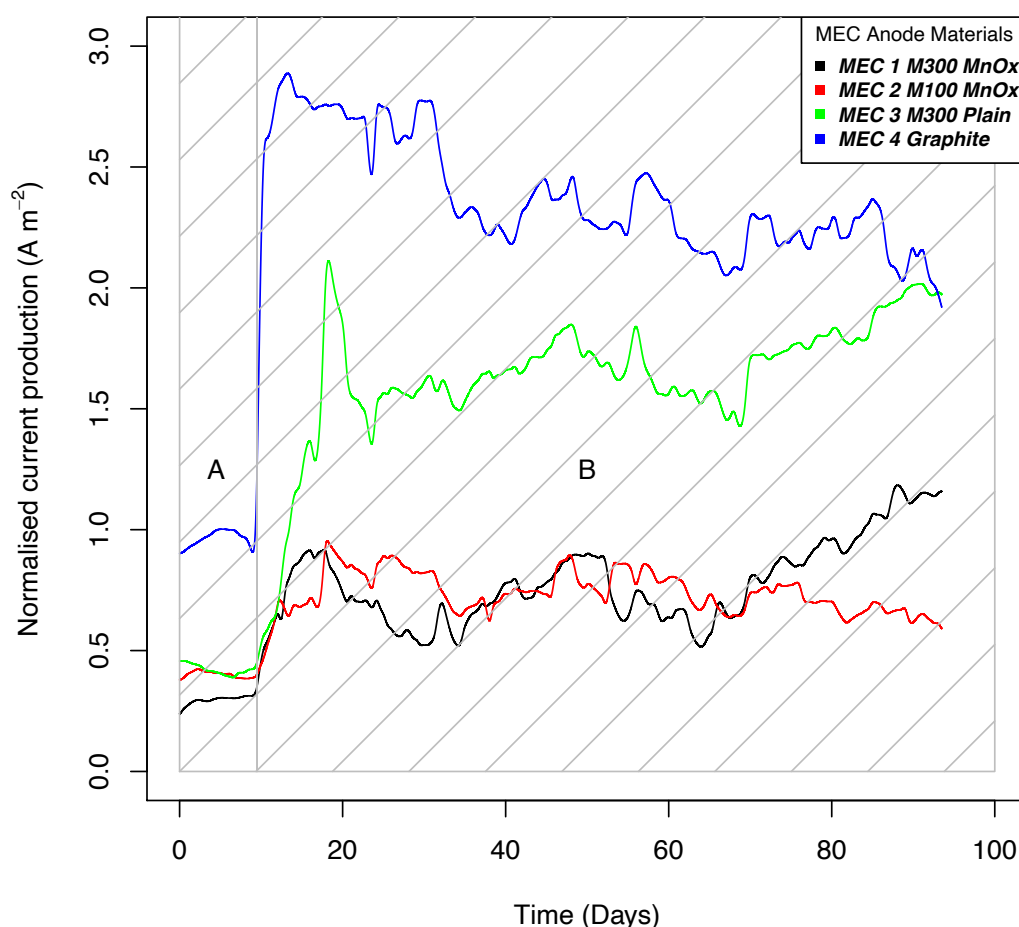


Figure 4-11: Current generation over time produced by the MECs over time

A: the initial period where a 1-ohm resistor was used to measure the current generation. B: the period from which the 1-ohm resistor was swapped out for a 0.1-ohm resistor due to the relatively low resistance of the MECs relative to the resistor.

It is expected that current generations would increase over time, as similarly to the smaller-scale MEC current increases (section 3.3.4) current increases in MECs should be due to an increase in electron donation from exoelectrogenic microorganisms which are oxidising substrates in the wastewater, so it bodes well for the recycled

carbon fibre that this was observed (in particular for MEC 1 and 3).⁴⁶ As MECs 1 and 3 are the thickest of the recycled carbon fibre materials (both M300) and have a less compacted structure relative to the graphite felt, it's possible that the increased current generation was due to an increased number of obligate anaerobes (many of which are exoelectrogenic such as *Geobacter* and *Shewanella*) relative to the thinner MnOx coated M100 and graphite felt.¹¹⁷ The explanation for the higher current of the M300 MnOx compared to the M100 MnOx in the latter stages of the trial will likely have been due to the increased surface area which in turn, would have more biofilm colonisation, resulting in more oxidation of wastewater substrates (and therefore a higher current). Why this wasn't the case earlier on in the trial is not clear, as it would be expected that the M300 MnOx would always have a higher current than a thinner version of the same anode. It is likely due to the microbial communities developing in different ways, with the thicker variant eventually producing more current/

MEC 3 had the second-highest current generation, constantly higher than MEC 1. In the more industrially appropriate running conditions in this trial, the addition of manganese (IV) oxide has resulted in a reduction in the overall current generation, which is explainable by the increased resistance which would be brought about by the coating ($\text{Current} = \text{Voltage} / \text{Resistance}$).⁹⁴ During the 90 days of operation, current generation, hydrogen production and COD removal has been negatively affected by the addition of manganese (IV) oxide, but due to the lower resistance, the overall running cost of the system will have been lower (investigated in section 5.3), which may be advantageous in the longer term.

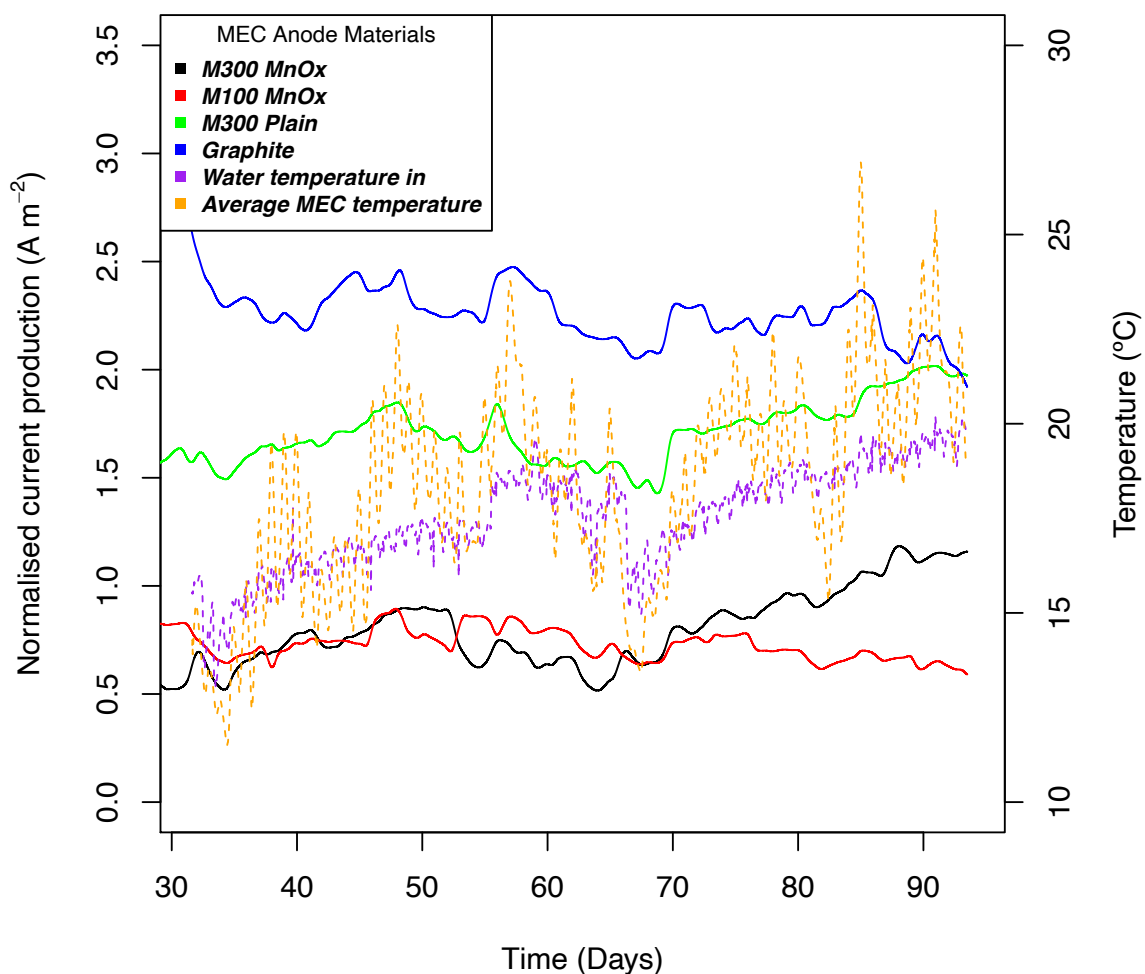


Figure 4-12: Normalised current generation for each MEC in relation to temperature

The temperature inside each of the MECs oscillated over the course of a day, with the current generations oscillating in a similar fashion (i.e. increasing temperature usually resulted in increased currents). The MECs being on average 5-8°C hotter than the input wastewater. The overall internal temperature of the MECs continued to increase over time. MECs 1 and 3 current generations had strong positive correlations with temperature (R-Values of; 0.67 and 0.71 respectively – see tables in section 8.2.3 in the appendix). MEC 4 had no correlation (R = -0.01) which is expected as the current generation was very high (highest overall) and did not seem to change with temperature. MEC 2 a weak positive correlation (R = 0.19) which from Figure 4-12 is expected, as the current did not change with temperature.

4.3.7 Efficiency calculations

The overall efficiencies of the MECs were very low for all subtypes of efficiency (energy recovery, coulombic and substrate efficiencies). However, MEC 3 (Plain M300) was consistently the best and MEC 4 (graphite felt) was consistently the worst).

Energy recovery efficiency was low for all of the systems, which in part was due to the use of 1 V to power the MEC. At 1 V, assuming no losses, the maximum theoretical energy efficiency recovery of 123%.⁴⁷ MEC 3 was still the best in terms of efficiency with 8%. The graphite felt MEC (MEC 4) had an efficiency <0.001%, which can be explained by the very high current generation and very low hydrogen gas recovery (Table 4-13). Due to the constant current increases and hydrogen productions observed, it's likely that the voltages used to run the systems (in particular for MECs 1 and 3) could have been reduced to improve upon the η_E . The production of H₂ would probably not have been reduced meaning the overall η_E would have been improved. However, even with reductions to the input power, changes to the architecture and method of H₂ recovery will be required to improve the η_E .

Table 4-13: Electrical energy efficiency values for the MECs

	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode Material</i>	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
<i>Electrical energy recovery for the whole MEC % ($\eta_{E_{mec}}$)</i>	5.00	0.00	7.89	0.00
<i>Peak electrical energy recovery for the whole MEC %</i>	12.00	0.00	20.00	1.87
<i>Highest average electrical energy recovery for a module of an MEC % ($\eta_{E_{mod}}$)</i>	11.00	0.00	13.00	1.73
<i>Highest peak electrical energy recovery for a module %</i>	28.53	0.00	37.50	6.12

Figure 4-13 shows how the ηE_{mec} changed over time, where the peak efficiency (over 20% for MEC 3) was around day 50, the time point at which hydrogen gas was highest and subsequently decreased. With regards to MEC 3, it was not temperature that affected the ηE , which was also the same for hydrogen production. It's likely that the proliferation of hydrogenotrophic taxa began to impact the performance, reducing H_2 recovery and therefore, the ηE .

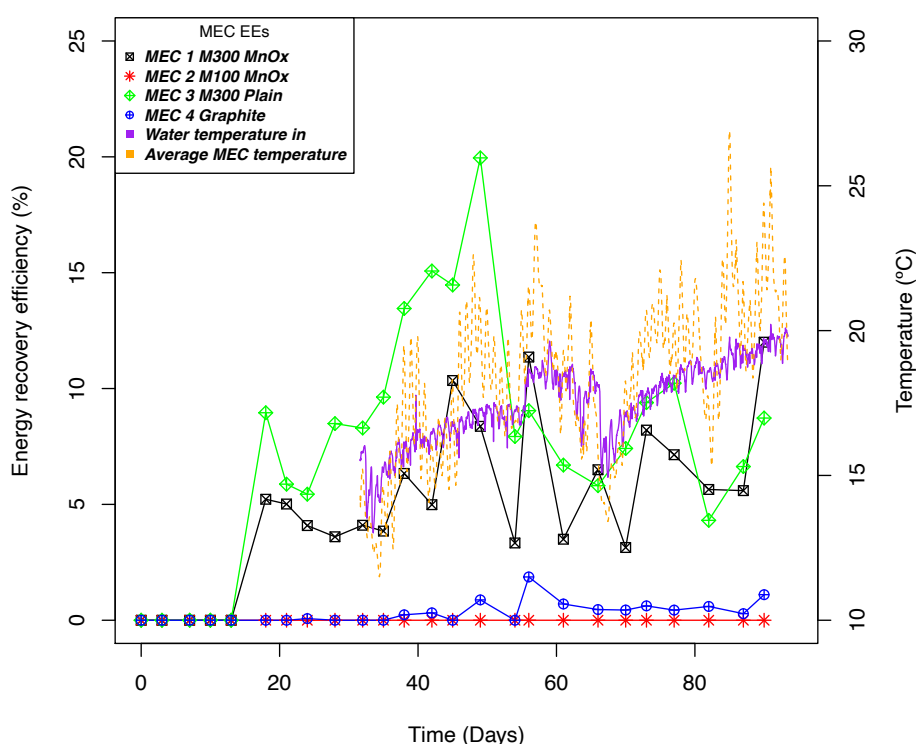


Figure 4-13: Electrical Energy efficiency of each MEC over time - temperature also shown

Coulombic efficiencies (CE) were low (<0.01-4.92%). MEC 3 was the best (4.9%) (Table 4-14). MEC 4 had less than 0.01% for the average CE_{mec} and just over 1% for the highest average from a module. The low coulombic efficiencies indicate that of the hydrogen gas being produced, the vast majority was being lost, supporting the notion that hydrogenotrophic taxa had proliferated, triggering the reduction in efficiency from day 50.^{73,76,143} Leakages are also very likely due to the small nature of hydrogen molecules. As there was a sudden increase in the amount of hydrogen gas produced for MEC 3, it is possible that the build-up of gas resulted in some rupturing of the glue that was used to fix the Entek membranes of the modules as well as to the tubing and connections for the gas bags.

Table 4-14: Coulombic efficiency values for the MECs

	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode Material</i>	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
<i>Total Coulombic efficiency for whole MEC % (CE_{mec})</i>	3.20	0.00	4.92	<0.01
<i>Peak Coulombic efficiency for the whole MEC %</i>	6.50	0.00	10.78	1.01
<i>Highest average coulombic efficiency for a single module % (CE_{mod})</i>	12.90	0.00	7.00	0.69
<i>Highest peak coulombic efficiency for a single module %</i>	19.30	0.00	20.25	3.92

The substrate efficiency (S_E) was highest for MEC 3 (Table 4-15), three times greater than MEC 1 (12% and 4% respectively), marginally higher than the coulombic efficiency. The low substrate efficiencies suggest that the oxidisation of the substrates is resulting in the production of other products (likely methane, hydrogen sulfide, etc.) by non-exoelectrogenic microorganisms, resulting in less H_2 production and recovery. This will be improvable with different architectures.

Table 4-15: Substrate efficiency values for the MECs

	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode Material</i>	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
<i>Substrate Efficiency for the whole MEC % (S_{mec})</i>	4.08	0	12.12	0.01
<i>Substrate Efficiency for best module (S_{mod})</i>	18.90	0	20.09	5.04

MEC 3 has the highest total efficiency ($\eta E+s$), followed by MEC 1. MEC 4 has below 0.01% (Table 4-16).

Table 4-16: Total energy efficiency for the MECs

	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode Material</i>	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
<i>Total energy Efficiency % ($\eta E+s$)</i>	2.08	0.00	4.62	<0.01

The very overall efficiencies are expected due to the low substrate and energy recovery efficiencies calculated previously. The losses in the system are very high across all MECs, suggesting that issues with architecture, losses (from multiple sources) and high energy input (1 V from power supply) are making the system very

inefficient. The architectures used here have been suitable to demonstrate and learn about the differences in performance between the different anodes, but larger-scale deployment the method of gas collection and operation requires refinement.

4.4 SEM images

All of the MECs have evidence of biofilm on the majority of their anodes (Figure 4-14). Due to a lack of a critical point dryer, the drying process has caused the biofilm to fall off in places but is still visible.

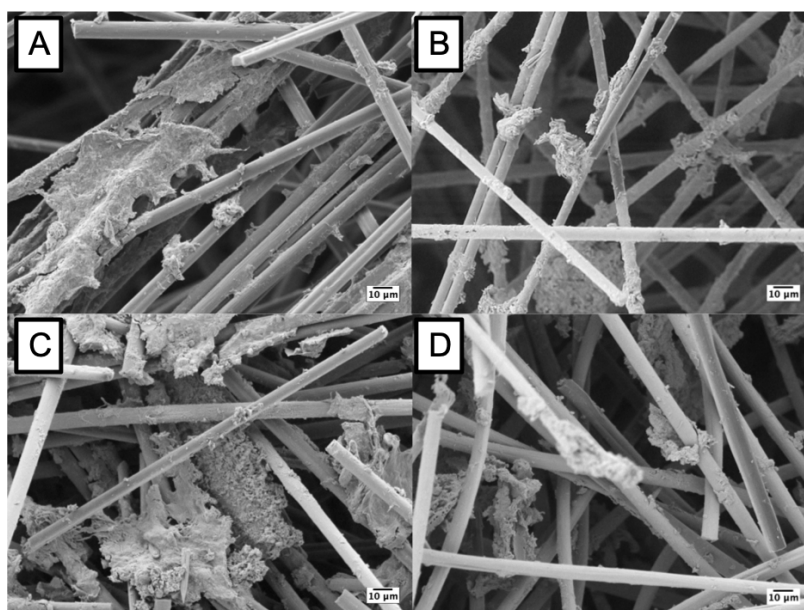


Figure 4-14: SEM of all MECs at 1000x magnification

A: MEC 1 – MnOx M300. B: MEC 2: MnOx M100. C: MEC 3 – Plain M300. D: Graphite felt.

Only module 2 from MEC 4 appears to have no biofilm coverage (Table 4-17). The coverage appears to be good on all of the other modules, with no significant difference's observable between the different anode materials (SEM images at 1000x magnification of every module are in the appendix in section 8.3).

Table 4-17: Presence and amount of biofilm under SEM for each module

		Module				
		1	2	3	4	5
MEC 1	MnOx M300	Yes	Yes	Yes	Yes	Yes
MEC 2	MnOx M100	Yes	Yes	Yes	Yes	Yes
MEC 3	Plain M300	Yes	Yes	Yes	Yes	Yes
MEC 4	Graphite felt	Yes	No	Yes	Yes	Yes

4.5 Innovation for MECs may lie with the use of recycled carbon fibre electrodes

From a purely functional perspective (i.e. did the materials allow for the production of hydrogen gas and wastewater treatment), three out of the four materials are suitable for use in an MEC – Mn (IV) oxide coated M300, Plain M300 and the SGL 4.6 graphite felt (already confirmed).⁶⁷ The Mn (IV) oxide coated M100 failed to produce any gas, therefore, it does not appear to be suitable for use in an MEC. This is likely due to its lack of surface area compared to the other three materials, meaning less biofilm was able to form over the surface of the anode to carry out the treatment of wastewater and sequestering of electrons (as well as proton production and subsequent reduction) to facilitate the hydrogen evolution reaction at the site of the cathode. Although less expensive than the MnOx M300, it failed to produce hydrogen and therefore cannot deliver the innovation required for industrial MEC deployment.

Taking this a step further, the question is: out of these materials, which of these present the greatest opportunity for successful deployment. If the number of functional modules is the determining factor, the choice is between the plain M300 and the SGL 4.6 graphite felt. However, if instead, it is the wastewater treatment performance and hydrogen gas production, the SGL loses to the plain and Mn (IV) oxide coated M300 anodes (and significantly worse overall).

The resistance increase provided by the presence of the manganese (IV) oxide is likely hampering the initial start-up performance of the MEC and therefore any benefit (observed from its use in Chapter 3 for the lab-scale experiments) has been lost when a power supply is used to apply a voltage instead of the voltage fixation by a potentiostat. Therefore, it would appear that the coating of manganese (IV) oxide on an anode for use in an MEC is unnecessary when considering the performance capabilities of the plain M300, which is cheaper and less environmentally taxing to produce, as there is no need for the coatings which uses the following chemicals; manganese (II) acetate, hydrochloric acid and hydrogen peroxide, as well as water and energy (heat and electrical). However, towards the end of the experiment, the performance of MEC 1 that used the M300 Mn (IV) oxide appeared to improve in terms of hydrogen production, as more modules began to produce high purity hydrogen gas,

triggered by the increase in biofilm brought about by the higher temperatures of the wastewater in the MEC.

The statistical significance values support the claim that the recycled carbon fibre is superior to the graphite felt used in this study (for wastewater treatment and hydrogen recovery – see Table 8-4 for P-values generated from R squared T-tests). Other known materials could also be compared (carbon felts, graphite plates and brushes)^{44,59,76} but to date, there are no materials that are as cost-competitive as the recycled carbon fibre anodes developed and used in the mini scale pilots.

Despite the results suggesting that the recycled carbon fibre is overwhelmingly superior to the graphite felt, the overall efficiency (energy recovery, coulombic, substrate and total) was still very low, even for the best performing system. It has been addressed that a large factor was the high voltage applied (1 V) which limited the maximum efficiency to 123%, therefore a lowering of this is required. If the hydrogen recovery is identical (in terms of moles) then the efficiency will improve. There would also have been losses, both leakages and from hydrogenotrophic microorganisms. Leakages will be reducible with different materials and better sealing of the systems, and more frequent gas recovery from the bags. The hydrogenotrophic microorganisms will be more difficult to control, as the membrane has been confirmed as being permeable to them.⁶⁷ More frequent replacing of the catholyte with sterile liquid may improve the performance (and would be required for industrial application) but this will increase the complexity of the system and potentially the capital cost. A bactericidal coating (metal oxides such as magnesium)¹⁴⁹ on the cathode could help to prevent hydrogenotrophs but it's long term efficacy and impact on hydrogen evolution will need to be considered. It was noted in Chapter 3, that anodes that had manganese (IV) oxide coatings had a lower abundance of sulfate reducing bacteria (SRB) which are known hydrogenotrophs. It is possible that this could help limit the proliferation of the SRB on the anode and therefore, decrease the likelihood of SRB contamination on the cathode.

4.6 Summary

Following the results of the upscaled MEC reactors, the use of the recycled carbon fibre as an anode has the potential to be disruptively innovative. The plain ELG

materials (M300) is significantly cheaper than the graphite felt per unit area. A life cycle analysis (LCA) of the use of the Carbisio M™ material is also far less damaging to the environment when compared to virgin carbon materials.¹⁰³ Naturally, this LCA does not use the graphite felt as a comparison, but the graphitisation process of carbon materials is very energy intensive and as it is a virgin material, its use compared to the recycled carbon fibre based anodes used in the upscaled MECs will have a greater environmental impact.⁸⁰

Finally, there is the benefit of price – both of the materials that outperformed the graphite felt were significantly less expensive than the graphite. As it is cost that is the main barrier to deploying this technology, this is likely to be the most significant argument for an innovative step. This suggests that now it is only the current collector that needs addressing in terms of the capital cost of an MEC.

Throughout this report (and the project), there has been a great deal of focus on the cost of the anode and the need to reduce this cost. It is with the reduction of this cost that will allow for the deployment of any type of large-scale BES for wastewater treatment. However, there are multiple components to an MEC that also have significant capital costs, all of which, will require review. A detailed analysis of the cost to build an MEC using the recycled carbon fibre will help provide a snapshot into the potential future of the MEC and how it compares to activated sludge pools. A comparison of the capital and operational costs over a defined period (e.g. 20-50 years) will give a true insight of how far the technology is from successful deployment.

5 Cost-benefit analysis of the use of the anodic materials

5.1 The importance of CapEx and OpEx relative to innovation

To deploy the MECs (and deliver on innovation), the technology must be affordable enough to deploy at large scales.⁷⁹ It has been shown that the recycled materials work very well in the larger-scale reactors, producing hydrogen gas and also treating wastewater by reducing the chemical oxygen demand of the effluent, as well as other nutrient concentrations. However, this must be price competitive with the other existing assets that are used for treating wastewater for the delivery of innovation.⁷⁸ If these products are to be disruptively innovative to the wastewater treatment industry, capital expenditure (CapEx) and operation expenditure (OpEx) must be comparable to that of an activated sludge pool (ASP). This will be critical if MECs are to deliver on their potential of a more sustainable method of wastewater treatment, which the industry (and indeed the world) is in need of.^{3,150}

To compare the total expenditure (TotEx) for the lifetime of a potential MEC to replace an ASP a size was selected for both assets. The size was based on a population equivalent of 50,000, meaning the asset would be able to treat the wastewater produced by a population of 50,000 people.¹⁵¹ As ASPs have been used for decades for wastewater treatment, Severn Trent Water was able to provide the CapEx, OpEx and TotEx estimations for an ASP designed for a PE of 50,000, to which the proposed equivalently sized MEC could be compared.

5.2 Capital cost comparisons – CapEx

The capital expenditure (CapEx) is the total price of the system, including materials, overheads and labour.¹⁵² The CapEx costs can be subdivided into civil and mechanical and engineering costs. The civil costs are defined as the expenditure to build the components that will last for the entirety of the assets life and do not require replacement. An example of this would be the channels of an activated sludge pool that are made from concrete. The mechanical and engineering costs (M&E) are defined as the components that do require replacing at different times. Using the activated sludge pool as an example again, the blowers used to aerate the wastewater are one such example, which require replacing every 10 years.¹⁵³ For the initial CapEx,

the M&E is included but the main requirement of these costs is for the total expenditure, which is detailed later.

5.2.1 Capital costs compared to other MECs

CapEx was first determined for all of the MECs used in Chapter 4 in multiple configurations for a population equivalent of 50,000. This included;

CapEx 1: The mini-pilot 10 L reactor MECs using the actual costs to build them (no economy of scale with bulk orders). This meant multiplying the total cost of the MEC by the number required to serve a PE of 50,000, which in this case was over 333 K MEC reactors.

CapEx 2: The mini-pilot 10 L reactor MECs using estimated economy of scales and lean manufacturing processes (prices for all components found online). As they were the same dimensions as in CapEx 1, 333 K MECs would be required.

CapEx 3: The predicted minimum reactor size costs (1000 L reactors), using the less expensive components from CapEx 2 and assuming the performance would scale from the smaller reactors (this is unlikely based on the comparison of increasing scales by *Cotterill et al.*).⁶⁷

CapEx 4: Using the same reactor size costs in CapEx 3 (1000 L reactors) but instead exchanging the current collectors proposed in CapEx 3 with the cost of those described in the *Heidrich* pilot.^{76,79} This CapEx also assumes scalable performance from the MECs used in Chapter 4.

Assumptions had to be made for the CapEx and OpEx calculations throughout. These are detailed in Table 5-1.

Table 5-1: List of assumptions for cost benefit analysis (CapEx, OpEx and TotEx).

Assumption	Reason
CaPex Labour costs are the same (in terms of proportional percentage) for MECs and ASP	A more effective method of determining the costs was not possible, so the assumed labour costs of 15% ¹ of the total CapEx were applied to the MEC.
Operational labour costs for both MECs and ASPs are the same	An assumption is made that the labour costs to operate an ASP are the same as an MEC.
Labour costs for capital expenditure are only for the civils component.	Complexity and difficulty to determine for the MECs, therefore the initial 15% costs are the only labour costs assumed in this analysis.
Energy input and cost per unit of energy will not change over time	Energy costs may (and most likely will) change over time. There is also the potential to reduce the units of energy used to operate the assets. This will not be taken into account for the OpEx and TotEx calculations.

The prices for each of the CapEx scenarios are detailed in Table 5-2.

Table 5-2: CapEx comparisons for the different materials excluding labour (values in millions of £)

Material	CapEx 1	CapEx 2:	CapEx 3	CapEx 4
<i>M300 MnOx</i>	158.62	27.31	4.86	4.46
<i>M100 MnOx</i>	157.56	26.56	4.67	4.27
<i>M300</i>	129.63	24.02	4.02	3.62
<i>Graphite</i>	171.32	40.78	8.29	7.89

Immediately, it is clear that scenarios 1 and 2 are significantly higher than CapEx 3 and 4, but crucially, significantly higher than the CapEx for the ASP (£3.2 million). Therefore CapEx 1 and 2 would not be appropriate for industrial application and cannot be considered, highlighting the need for an economy of scale for MEC technology.⁷⁹ CapEx 3 and 4 are significantly closer to the £3.2 million ASP CapEx.

The CapEx 4 scenario was selected for further development (operational and total expenditure) as it had the lowest overall cost and was the closest to the £3.2 million

¹ 15% assumption from conversations with Capital delivery and Treatment Process team members at Severn Trent

cost of the ASP. Furthermore, only MnOx M300 and M300 anode material MECs were selected from this scenario for two principal reasons:

1. They produced the most hydrogen gas and had the best quality effluents. Furthermore, the M100 MnOx failed to produce any hydrogen gas so it would not result in a functional MEC.
2. The graphite felt MEC is more than double the cost of the plain M300 MEC and close to double the cost of the M300 MnOx MEC.

Using the 15% of capital cost assumption as labour, the additional costs were determined as being £0.64 million and £0.75 million for the M300 and M300 MnOx MECs respectively. The MnOx M300 MEC is more expensive due to the blanket 15% assumption, which will be discounted (there is no justification for the asset to have a more expensive labour capital cost component), therefore the £0.64 million cost will be used for all total capital costs going forward. The finalised capital costs for the M300 and M300 MnOx are; £4.3 million and £5 million respectively.

The anode cost has had a very large impact on the overall cost of the system, with the plain M300 costing £5.52 per m² and the graphite felt costing £88, this is over a 93% saving (and over 98% when compared to the Olmec used in the *Heidrich et al.* pilot)^{76,79}. The cost of manganese (IV) oxide deposition was determined to be £8.40 per m² of anode (see appendix section 8.4.1 for details), which would result in a total cost of £13.9 for a m² MnOx M300 anode, which is still significantly less expensive than the graphite felt anode.

Though not used for further cost comparisons, if the example MEC used by *Aiken et al.* replaced the Olmec carbon felt with the M300 recycled carbon fibre, an estimated £31 million pound saving is possible (£42.3 million – £11.2 million = £31.1 million), changing the breakdown of the costs dramatically (Figure 5-1).

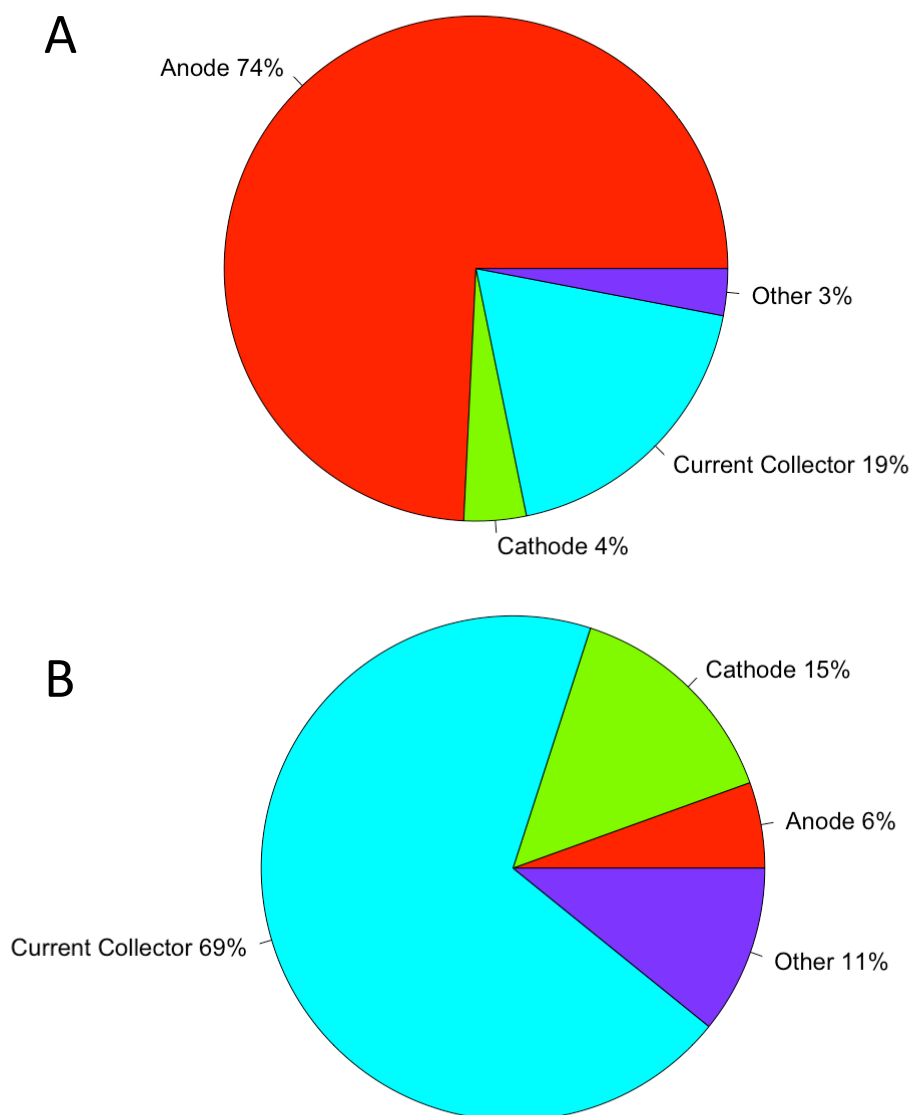


Figure 5-1: Cost percentage breakdown for the Heidrich pilot determined by Aiken with the Olmec (A) and M300 (B) anodes.

N.B. 'Other' encompasses: hydrogen tanks, piping/tubing, membranes and cassettes of the modules.

5.3 Operating cost comparisons – OpEx

By using the data current data and known voltage application from the experiments described in Chapter 4, the amount of power in (kWh) was determined for the plain

M300 and MnOx M300. This also took into account the general running costs (e.g. use of pumps, general maintenance, staff costs) which was based on the running costs of an ASP without the use of the blowers which was provided by Severn Trent Water. Included in the OpEx costs was the savings from the energy recovery from the use of hydrogen in a hydrogen fuel cell as well as the extra costs of replacing the catholyte. The detail of how this was determined is in the appendix in section 8.4.2, with the final costs detailed in Table 5-3.

Table 5-3: Final OpEx cost savings

Device	OpEx (£)	% Saving vs ASP
ASP	520,000.00	N/A
MEC M300 MnOx	342,641.31	34.11
MEC Plain M300	350,627.48	32.57

The energy cost savings (including the recovery of hydrogen gas) are £169 K and £177 K for MEC M300 and MEC M300 MnOx, respectively. Using the CapEx's determined previously and the relevant OpEx, the total expenditure scenarios were then determined.

5.4 Total life cycle cost comparison – TotEx

The total expenditure (TotEx) is the combination of CapEx and OpEx throughout a predetermined period of time. Usually, the TotEx is in years to represent the lifetime of the asset, which for wastewater assets can be between 25-50 years. As was alluded to in section 5.2, the mechanical and engineering costs (M&E) can become a significant cost for the TotEx of the asset, as they may need replacing multiple times throughout the life time of the asset.¹⁵³

An accurate TotEx for an MEC (to the level of existing wastewater treatment assets) has not yet been determined (there are no MECs that have been used for 5 years or more), so four different scenarios were developed and compared to the known TotEx for an activated sludge pool. The TotEx scenarios were as follows:

TotEx ASP: Costs of the ASP are provided by Severn Trent and include the civils, M&E and operational expenditures for the duration of 50 years.¹⁵⁴

TotEx 1: Costs of MECs assuming that all components excluding the tank are replaced every five years. This includes; current collectors, anodes, module casing, membrane and fittings.

TotEx 2: Costs of MECs assuming that all components excluding the tank are replaced every 10 years. The components replaced are the same as those in TotEx 1.

TotEx 3: Costs of MECs assuming that the current collectors and the plastic casing of the modules do not need replacing. All other components do, excluding the tank. The stainless-steel current collectors were excluded as stainless steel 316 grade can have up to a 50 yearlife time in water and wastewater conditions, so in theory, this should not require replacing at the same rate as the other components.¹⁵⁵

TotEx 4: Using costs of TotEx 3 with an overall 25% increase to the cost. This takes into account any oversights or increasing costs of materials, labour, etc.

The TotEx 50 (50 years) are listed in Table 5-4.

Table 5-4: TotEx 50 list comparison

TotEx list	MEC MnOx M300 (millions £)	MEC M300 (millions £)
<i>TotEx 1</i>	56.4	48.4
<i>TotEx 2</i>	37.4	33.6
<i>TotEx 3</i>	29.7	25.9
<i>TotEx 4</i>	37.1	32.4

Compared to the TotEx of the ASP (£32.40 million – value from Capital Delivery team at Severn Trent)¹⁵⁴ the 3rd and 4th scenarios look promising for the MECs. Assuming the model is reliable, both MECs cost less than the ASP over 50 years. However, if a stress test is applied (a 25% increase in cost - scenario 4) only an MEC using plain M300 has a TotEx that is equal to the ASP. The MnOx M300 MEC is over £4 million more. Figure 5-2 shows how the TotEx's compare over 50 years for an MEC using plain M300 as the anode.

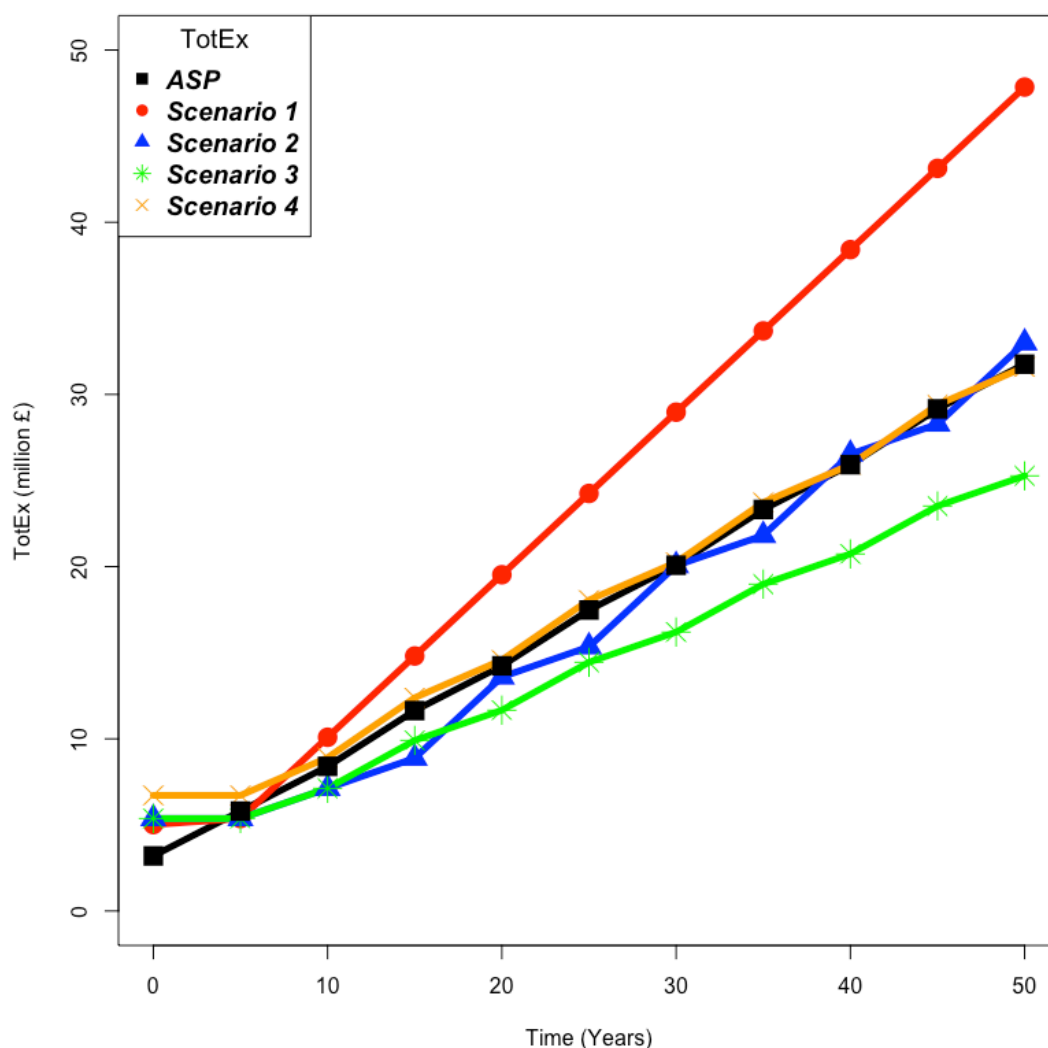


Figure 5-2: TotEx comparisons of the ASP and MEC scenarios

5.5 Improvements required

Further cost savings from the operation of the MEC will be very beneficial. The MECs tested in Chapter 4 used 1 V from the power supply, severely limiting their efficiency. This means that a lower applied voltage would have treated the wastewater to the same standard as well as producing the same quantity of hydrogen gas, which would have resulted in some potentially large financial savings.

The other issue to address is the recovery of hydrogen gas as this would have lowered the operational costs due to the value of the gas. Coulombic efficiency calculations (Section 4.3.7) indicated that losses were likely occurring (e.g. from leakage and hydrogenotrophic microorganisms). Architectural improvements to recovery hydrogen

will improve the OpEx and potentially, operational changes to reduce microbial proliferation on the catholyte.

What has not been considered in the cost-benefit analysis is the wastewater treatment performance of the MECs that requires significant improvement. If it is assumed that the MECs would require a secondary treatment stage, an extra TotEx for another asset would be required. Alternatively, alterations to the operation and architecture of the MECs used in Chapter 4 would be required to improve the wastewater treatment efficacy, which could impact the cost of building and running the MEC.

5.6 Summary: potential innovation lies with the use of recycled carbon fibre as the anode – but not alone

The only way to deploy an MEC at scale will be when it becomes cost-competitive to do so when compared the standard options deployed at STWs (i.e. ASPs, trickling filters) . Compared to the larger and smaller-scale systems in the literature that have used virgin graphite and carbon materials of varying compositions for the anode, the recycled carbon fibres assessed in this cost-benefit analysis are significantly less expensive.⁷⁹

The cost saving achieved by using the recycled carbon fibre is so large that, assuming comparable performance, there is a strong argument against using the virgin materials in any larger-scale MEC for wastewater treatment. Only one graphite type material was tested in the larger-scale MECs in Chapter 4 (as it was known to work as an anode and was significantly cheaper than many other known graphite/carbon felts) so other materials tested in the literature could still outperform the recycled carbon fibres. However, the recycled carbon fibre materials performed significantly better and were 96% less expensive. At scale up, this resulted in a CapEx material saving of over £3.6 million (a 50% saving) compared to an MEC using graphite.

Arguably, compared to other MEC pilots, the use of recycled carbon fibre could be disruptively innovative, as the cost-saving is so large. The TotEx calculations suggest also that the deployment of MECs is a possibility with the recycled carbon fibre (being both disruptively and radically innovative).

Despite the cost savings possible from the use of the recycled carbon fibre and the advantages (both in terms of price, sustainability and operational costs), the MECs all showed poor wastewater treatment relative to activated sludge pools, which is the main parameter that requires improvement from the MECs deployed in this project. Better removal has been reported in the literature (with the same type of the graphite felt used in the Chapter 4 MECs– SGL GFD 4.6)⁶⁷ suggesting that it is architecture (and potentially scale) that was effecting the COD removal of the MECs and not the use of recycled carbon fibre.

6 Conclusion

6.1 Overall significance of all results

Wastewater treatment requires large overhauls to its practices if the is to become more environmentally and economically sustainable. The technology exists to process wastewater effectively to protect populations from pathogens and the environment from damage, yet much of the world's wastewater is released to the environment untreated and many people are forced to use dirty (and dangerous) water for drinking and hygiene. The cost of wastewater treatment is not only harming the environment actively, due to the burning of fossil fuels to power the assets, but it's capital and operational costs are beyond affordability for developing nations.

Numerous potential technologies are being investigated and developed to improve on the sustainability of the wastewater treatment industry. Working with the ISLE group in Italy, a UK based water and wastewater technology consultancy group, the main gained knowledge from where the numbers of potential wastewater sludge destruction technologies, which could reduce the cost of wastewater treatment, by processing sludge more efficiently and by producing products with higher value. There are examples of pyrolysis and gasification pilots with technology readiness levels (TRL) of 7-9, that are becoming increasingly more efficient. Their main failure, however, is that these technologies are trying to deal with the problem by-product of wastewater treatment (sludge production) instead of trying to solve the fundamental problem of sludge production in the first place. These technologies also do not reduce the energy demands of secondary wastewater treatment, namely from activated sludge pools.

The technology that is stopping wastewater treatment from becoming sustainable is the very energy intensive (albeit effective) activated sludge pool. This asset must be significantly improved in terms of energy use due to the nature of how it works (constant aeration of wastewater) there is only so much that can be gained from iterative improvements to the efficiency of operation of the blowers of an ASP. A dramatic overhaul or alternative solution is required, especially if large scale wastewater treatment is to be deployed in regions with poor wastewater treatment infrastructure.

MECs have the potential to solve this problem but improvements to multiple aspects of the technology are required. Arguably, the work in this innovation report will encourage larger-scale experimentation and deployment of pilot-scale MECs as major cost savings have been achieved while performing better than a tried and tested graphite felt used in a larger-scale pilot MEC.

By first assessing what the major barrier to deployment is (capital costs attributed to the anode) materials have been investigated and developed as potential MEC (and MFC) anodes to replace virgin graphite or carbon felts. Initial experiments have shown that the materials are functional as electrodes in electrochemical systems (batteries, fuel cells, electrolysis cells) demonstrated by their ability to produce currents and facilitate electrochemical reactions on their anode surface. Lab-scale experiments, though being inefficient in terms of energy recovery, demonstrated that biofilms could be sustained on the recycled carbon fibre anodes and that hydrogen gas was producible. 16S sequencing suggested that the recycled carbon fibres resulted in small changes to the abundance of certain genera of microorganisms. A reduction of *Geobacter* abundance due to the presence of manganese (IV) oxide (or a relative abundance of them when it's not present) does not seem to have resulted in negative performance and appears to have stimulated the growth of different types of exoelectrogenic bacteria, namely *Arcobacter* genus. There has also been a reduction in sulfate reducing bacteria in manganese (IV) oxide coated anode biofilms, suggesting that the oxide has either; directly dissuaded the growth of SRB or has encouraged the growth of different microorganisms which are competitors with SRB.

Scale up yielded very promising results for the recycled carbon fibre anodes, producing significantly more hydrogen gas than an MEC using graphite felt. Furthermore, the MEC using the plain M300 performed best and also treated the wastewater significantly better than the MEC using graphite felt. In terms of cost-benefit, the predicted total expenditure of an MEC using the recycled carbon fibre was not only significantly less expensive than an MEC using graphite felt but was also cost comparable to an activated sludge pool. Despite the potential limitations of the cost benefit analysis, the savings attributed to the use of recycled carbon fibre as an anode have potentially enabled for much larger MECs to be constructed at pilot-scale to

prove to water companies that MECs can replace the less efficient and unsustainable assets used today, which would be an example of disruptive and radical innovation.

Despite the positive results of this research, there are issues that need to be addressed, namely performance and operational costs. Lowering the voltage used to run the MECs would dramatically increase the energy recovery and coulombic efficiencies, as less energy would be used to run the system for theoretically, the same hydrogen recovery. The substrate efficiency requires improvement and when combined with the low energy recovery and coulombic efficiency, indicates that losses of hydrogen to hydrogenotrophic bacteria (reported in multiple small and larger-scale MECs) and losses from leakages require significant reductions. The MECs must be able to treat wastewater to a higher standard than what was possible from the upscaled variants described in Chapter 4.

The larger-scale cost comparisons and estimations bode well for the future of MECs, showing the use of the recycled carbon fibre anode has been very significant in reducing the cost and therefore, bringing the technology closer to deployment. Based on the findings described in this Innovation Report, the cost reductions have the potential to be an essential component of any future MEC. The electrodes used here are carbon-based and therefore; conductive (while being derived from a waste material). This results in a very inexpensive and environmentally sustainable anode which, in terms of price, no other example of a carbon-based electrode that is commercially available can be found. This renders other anode materials inferior from a cost and sustainability perspective and in terms of performance, the results are promising. This adds further weight to claim that the use of the recycled carbon fibres as anodes in MECs would result in innovation as using other carbon-based materials make the technology unviable due to cost.

Despite the positive outcomes of cost reduction that have been demonstrated by this innovation report, the technology is still not ready for deployment and does require additional work to confirm the technology's potential and also to iterate and determine the ideal architecture and optimal non-anodic components. Based on the findings from this Innovation Report and literature examples, the new cost limiting component of the MEC is now the current collector.

A summary of the how the initial aims of the project that were outlined in the introduction of this report have been addressed and how they contribute to science and industry.

Table 6-1: Research aims and contributions to science and industry

Aim	Contribution to Science	Contribution to Industry
Identify a suitable anode materials that is inexpensive – achieved via the use of recycled carbon fibres	<ol style="list-style-type: none"> 1. Encourage focus of academia on other material components of electrochemical systems that require cost reduction or trying to improve upon the embodied climate change potential of the material i.e. current collectors, membranes etc. 2. Inexpensive nature of material should encourage more research into the area for larger scale applications due to the significantly reduced costs. 	<ol style="list-style-type: none"> 1. A use for a waste material that would otherwise be disposed of in landfill. This in turn, will valorize the material. 2. The diversion of any materials from landfill will reduce the operational costs of the producer of the waste carbon fibres.
Demonstrate inexpensive material is functional in an MEC – achieved via the use of recycled carbon fibres and successful electrodeposition of manganese oxide.	<ol style="list-style-type: none"> 1. Different anode materials resulted in biofilms having different relative abundances of different genus of microorganisms (including electrogenic genera). 2. Manganese oxide electrodepositions appeared to negatively influence the proliferation of sulphate reducing bacteria – a phenomenon that should be further explored as there are potential real world applications for this. 	<ol style="list-style-type: none"> 1. For the water industry, the production of hydrogen sulphide from sulphate reducing bacteria is hazardous to human health and results in the damaging of assets. The use of manganese oxide appears to stem their proliferation – this could be a simple and cost effective method of reducing hydrogen sulphide production, resulting in a net capital and operational saving.
Upscaling of the MEC – achieved	<ol style="list-style-type: none"> 1. MECs will benefit from further research and investigation at lab, bench top and pilot trial before they are deployed as wastewater treatment assets. Therefore, the successful demonstration of recycled carbon fibres (which remove the anode 	<ol style="list-style-type: none"> 1. Demonstration that large capital cost savings of MECs are possible with the use of recycled carbon fibre anodes. 2. Demonstration that hydrogen gas recovery is possible from sewage using MECs and that the least expensive version of MEC had the best performance in that regard

	as the major cost barrier of the technology) will encourage researchers to investigate other elements of MECs that must be addressed for deployment (i.e. architecture, membrane use, sewage feed, voltage supply etc.).	(there is growing increase in interest for hydrogen gas production from sewage treatment technologies by the water industry. 3. Demonstration that the best performing MEC was not impacted negatively by changing temperature, indicating that hydrogen production and COD removal is possible during warmer and colder periods.
Cost benefit analysis of the upscaled MECs	1. Improved appreciation and understanding of the importance of cost benefit analysis and the importance for scientific discoveries to have economic and social benefits to society.	1. Potential of MECs to cost competitive with existing wastewater treatment assets that are currently employed on sewage treatment works. 2. Demonstration of operational cost savings due to the lower energy usage of an MEC compared to an ASP (as well as the lower operational carbon emissions of the MEC over the ASP).

6.2 Suggested future work to move closer to the deployment of MECs

To get MECs closer to deployment, the following four areas would appear to be key areas for investigation:

1. Attempts to address the issue of solids retention within the reactor and to confirm whether scale is having an impact on this (i.e. does increasing the scale/changing the dimensions of the reactor change the settling time). It is possible that a desludging mechanism will be required or a longer HRT.
2. Any further reductions to capital costs for the current collector and confirming the reactor vessel (tank).
3. Improvements to wastewater treatment performance.
4. A life cycle assessment of the MEC, including its construction and operation, relative to an activated sludge pool. This will be important to confirm whether

an MEC does result in a positive environmental impact relative to an activated sludge pool.

With more understanding of these four areas, there will be a strong argument to build the systems at m³ scales and demonstrate the cost of doing so (capital and operational costs).

6.3 The importance of sustainable business practices

The need to continue to develop environmentally sustainable business practices for all industries is now vital if the effects of climate change are to be prevented. Humans depend on the environment for the economy as well as health and well-being, so it is in the interest of humanity to take measures to prevent man-made climate change and the associated negative impacts this has. The water industry has a relatively low global impact in terms of carbon emissions (compared to transport, aviation or animal agriculture) but within more developed economies, the potential carbon savings can be quite substantial. The reason the wastewater treatment industry has a low global impact is in part due to a lack of developed wastewater treatment infrastructure. Many developing economies cannot afford the running costs associated with wastewater treatment, resulting in untreated wastewater discharges to the environment. If a method of treating wastewater is developed at a significantly lower cost (either due to lower input costs or the benefit of an output of value) more wastewater will be treated globally, protecting natural water sources from untreated discharges. Sustainable business practices do not just revolve around improving the environment at the expense of economic or social sustainability. Instead, they should encompass all three, and should not have a negative impact on the economy or societal well-being. These challenges for all industries, not just the water sector, must continue to be investigated if humans, and indeed all other species, are to continue to thrive and enjoy a good standard of living.

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8 Appendices

8.1 Submission 3 Data

8.1.1 Wastewater Data from lab scale MECs

Table 8-1: Wastewater input data

<i>Wastewater input date</i>	<i>Day</i>	<i>COD concentration input (mg L⁻¹)</i>	<i>Reactor cycles per day</i>	<i>Days</i>	<i>Total COD input (mg)</i>
17/06/2018	0	565	1	5	28.25
22/06/2018	5	409	2.4	5	245.4
27/06/2018	10	387	2.4	5	232.2
02/07/2018	15	300	2.4	2	72
04/07/2018	17	335	2.4	5	201
09/07/2018	22	332	2.4	4	159.36
13/07/2018	26	329	2.4	3	118.44
16/07/2018	29	408	2.4	2	97.92
18/07/2018	31	386	2.4	2	92.64
20/07/2018	33	339	2.4	3	122.04
23/07/2018	36	441	4.8	2	211.68
25/07/2018	38	432	4.8	2	207.36
27/07/2018	40	485	4.8	3	349.2
30/07/2018	43	423	4.8	2	203.04
01/08/2018	45	326	4.8	5	391.2
06/08/2018	50	330	4.8	4	316.8
10/08/2018	54	329	4.8	3	236.88
13/08/2018	57	418	4.8	4	401.28
17/08/2018	61	269	4.8	4	258.24
21/08/2018	65	290	4.8	3	208.8
24/08/2018	68	210	4.8	4	201.6
28/08/2018	72	381	4.8	3	274.32
31/08/2018	75	339	4.8	3	244.08
03/09/2018	78	447	4.8	4	429.12
07/09/2018	82	643	4.8	4	617.28
11/09/2018	86	387	4.8	4	371.52
15/09/2018	90	362	4.8	3	260.64
18/09/2018	93	416	4.8	3	299.52
21/09/2018	96	405	4.8	4	388.8

25/09/2018	100	434	4.8	7	729.12
02/10/2018	107	406	4.8	4	389.76
06/10/2018	111	398	12	4	955.2
10/10/2018	115	367	4.8	6	528.48
Total COD mg					9843.17
Total COD g					9.84317

8.1.2 Efficiency calculations

Energy recovery efficiency

The electrical energy input (in Joules) is calculated as:

$$\text{Equation 8-1: } W_E = IE_{PS}\Delta - I^2R_{ex}\Delta t$$

This equation relates the energy input W_E to the current (I in Ampere), the average voltage applied to the system (E_{PS} in Volt) and the time lapsed (Δt in seconds). Additionally, it assumes that the current is measured over an external resistor (R_{ex} , in Ohm) which requires additional input of power, but as this is for measurement purpose and not consumed by the actual electrochemical system itself it is subtracted for common power balance calculations. In the present experiment, a potentiostat was used which reports the current without applying an additional, external resistor. Therefore, the $I^2R_{ex}\Delta t$ portion of the equation was not required, and the following equation was used:

$$\text{Equation 8-2: } W_E = IE_{PE}\Delta$$

The determination of E_{PE} required extra consideration, as a 3-electrode system was used for potentiostatic control (i.e. set potential between working and counter electrode), and the total applied voltage for electrochemical reaction (i.e. between working and counter electrode) was not recorded by the potentiostat. Thus, representative counter electrodes were assessed separately by determining their current-voltage relationship (I - V -curve) in the same electrolyte as used for the MEC experiments (i.e. 100 mM NaCl).

The output of energy from an MEC (W_{out}) in the form of hydrogen is here determined as energy that can be released from reacting the hydrogen in turn with oxygen (e.g. atmospheric) to water, such as it would be possible to do in a fuel cell. The energy that

can be released from this reaction is calculated by multiplying the moles of hydrogen produced in the MEC (N_{H_2} in (mol H_2)) by the standard higher heating value of hydrogen-oxidation with oxygen ($285.83 \text{ kJ mol}^{-1} H_2$), with liquid H_2O as reaction product, which is equivalent to the standard reaction enthalpy of the reaction of 1 mol H_2 with 0.5 mol O_2 to 1 mol H_2O , under standard conditions (i.e. 1 bar pressure, 25 °C temperature)^{156,157}. The formula for the energy calculation is shown in Equation 8-3:

$$\text{Equation 8-3: } W_{out} = 285.83 \Delta N_{H_2}$$

With the W_{out} and the W_E determined, the efficiency of the energy recovery, ηE (as a percentage), can be calculated, as shown in Equation 8-4:

$$\text{Equation 8-4: } \eta E = \frac{W_{out}}{W_E} \times 100$$

Coulombic efficiency

The amount of hydrogen recovered, compared to the theoretically recoverable amount from the total current that passed through the MEC, is referred to as the coulombic efficiency. Equation 2-5 is used to calculate from the current the amount N_{CE} (in mol H_2) of hydrogen that could have been produced from the current.

$$\text{Equation 8-5: } N_{CE} = \frac{I \Delta t}{2F}$$

I (in Ampere) is the current recorded from the potentiostat, Δt (in seconds) the time lapsed. Note that the current (in Ampere, A) is defined as the number of charged (in Coulomb, C) per second (s), thus $1 \text{ A} = 1 \text{ C} \cdot \text{s}$. From the charge transferred, the number of electrons transferred can be inferred by division by the Faraday constant ($F = 96,485 \text{ coulombs/mol electrons}$). The factor 2 in equation 2-5 relates to the fact that 2 mols of electrons are required for the formation of 1 mol H_2 .

The Coulombic efficiency CE (unitless) is calculated by dividing the N_{CE} by the moles of hydrogen collected (N_{H_2} in mol H_2).

$$\text{Equation 8-6: } CE = \frac{N_{CE}}{N_{H_2}}$$

Substrate efficiency: hydrogen production related to COD removal

The substrate efficiency is here defined as the quantity of hydrogen (in moles) recovered from COD-removal. COD is a measure of oxygen required for the oxidation of a complex substrate mixture such as wastewater. Oxygen, O₂, can take up 4 electrons for the reduction of water. With a molecular weight of 32 g mol⁻¹, a COD of 1 g consumes 0.03125 mol O₂ equivalent to delivering 0.125 mol electrons. The production of 1 mol hydrogen (H₂) from protons (H⁺) requires 2 mol electrons, thus 1 g COD allows at maximum the formation of 0.0625 mol H₂. This means the reduction of COD can be determined upon treatment, by subtracting the output COD from the input COD and therefore, the theoretically recoverable H₂ from COD (N_s in mol) is determined via Equation 2-7.

$$\text{Equation 8-7: } N_s = 0.0625 \Delta COD$$

The substrate efficiency (S_E , %) is then calculated from the actual recovered (N_{H_2} in moles) and estimated H₂ with:

$$\text{Equation 8-8: } S_E = \frac{N_{H_2}}{N_s}$$

Determining the total voltage applied across the whole system using a potentiostat

The voltage applied across the whole system has to be estimated from the fixed +0.4 V vs. Ag/AgCl set potential, applied by the potentiostat. As the potentiostat did not report the voltage it set between the working and counter electrode to maintain the desired potential between the working and reference electrode, the performance of the counter electrode itself was analysed in terms of current-voltage relationship (*I*-*V*-curve). Experiments were carried out with representative steel counter electrodes in the intended catholyte (0.1 M NaCl) as electrolyte.

1. A potentiodynamic scan for the steel electrode (potential set against Ag/AgCl reference electrode) to infer the voltage dependent kinetics of the hydrogen production reaction. The potentiodynamic scan was carried out from 0 to -1.2 V vs. Ag/AgCl at a scan rate of 0.05 mV/s.

2. The I-V-curve from step 1 was fitted with an exponential (Butler-Volmer) nonlinear least square (nls) function in R. Since hydrogen production was the desired reaction, the focus was on the region where this reaction is expected (theoretical standard potential of hydrogen formation at pH 7 is -0.413 V vs SHE, but since the product concentration (H₂) is low in ambient air, the corrected potential was -0.228 V). The output of the fitting were variables for the Butler-Volmer equation, namely the anodic coefficient a_c (related to the cathodic coefficient c_c by $a_c + c_c = 1$) and exchange current coefficient. The Butler-Volmer equation is as follows:

$$\text{Equation 8-9: } j = j_o \cdot \left\{ \exp \left[\frac{a_c z F \eta}{RT} \right] - \exp \left[-\frac{c_c z F \eta}{RT} \right] \right\}$$

3. For the MEC experiment, the currents recorded at set anode potential (vs. Ag/AgCl) had to at all times be equivalent to the cathodic current, thus the voltage necessarily had to adjust to the required potential (vs. Ag/AgCl) for a certain cathodic reaction rate. To estimate the cathodic voltages during MEC operation, the Butler-Volmer equation with fitted parameters was used to calculate cathodic voltages from the MEC currents. The cathodic, predicted voltages were then averaged for the entire duration of the experiment.
4. With the anodic voltage (vs. Ag/AgCl) being set and constant, and the cathodic voltage predicted, the average total voltage difference (working to counter electrode) during MEC operation was calculated according to Equation 6-1.

$$\text{Equation 8-10: } E_{PE} = E_P + E_E$$

E_{PE} is defined as the total applied voltage across the whole system. E_P is the known voltage applied from the potentiostat against the reference (400 mV vs. Ag/AgCl). E_E is the estimated average cathodic voltage (vs. Ag/AgCl).

8.1.3 DNA Data

Table 8-2: Average genus abundances for each MEC identified by 16S when a genus was over 1% for a sample (%)

	MEC number							
	1	2	3	4	5	6	7	8
<i>Genus below 1 in all MECs %</i>	36.01	30.56	39.17	34.83	34.59	33.31	35.71	36.85
<i>Vitellibacter</i>	3.82	0.69	0.20	0.54	0.27	0.29	1.00	0.04
<i>UBA6140</i>	2.08	0.43	0.84	0.83	0.05	0.14	0.33	0.73
<i>Bryobacter</i>	1.87	0.69	0.27	0.62	0.24	0.26	0.62	0.37
<i>Brevundimonas</i>	1.30	0.93	0.85	0.50	0.10	0.30	0.27	0.40
<i>Pseudorhodoplanes</i>	1.18	0.66	0.63	0.75	0.21	0.37	0.78	0.59
<i>Nitrosomonas</i>	0.70	0.21	1.17	0.46	0.99	0.93	0.79	0.80
<i>Paludibaculum</i>	0.27	0.47	0.61	0.54	0.46	0.49	1.08	0.64
<i>Leucobacter</i>	0.24	0.33	1.48	0.46	0.78	0.75	0.54	0.62
<i>Ferritrophicum</i>	0.20	1.87	0.57	0.47	0.15	0.53	0.09	0.41
<i>Ellin6067</i>	0.20	0.56	0.32	1.29	0.42	0.74	0.99	0.63
<i>Sulfurimonas</i>	0.14	1.29	0.39	0.16	0.79	0.87	0.21	0.95
<i>Azoarcus</i>	0.04	0.68	0.90	0.59	0.05	0.31	0.34	1.09
<i>ADurb.Bin063-1</i>	2.41	0.80	0.63	1.35	0.57	0.69	0.45	0.67
<i>OLB8</i>	2.01	0.29	0.53	1.24	0.06	0.05	0.69	0.40
<i>Ignavibacterium</i>	1.27	1.19	0.28	0.35	0.38	0.36	0.70	0.40
<i>Oligotropha</i>	1.03	0.71	0.93	1.50	0.09	0.38	0.30	0.59
<i>Dechlorosoma</i>	0.20	1.13	0.24	0.57	0.46	1.10	0.66	0.28
<i>Desulfobacter</i>	0.06	0.73	0.63	0.29	1.46	1.09	0.54	0.98
<i>Desulfomicrobium</i>	0.05	0.50	0.59	0.32	1.43	1.45	0.30	0.92
<i>Beggiatoa</i>	0.00	0.00	0.00	0.00	0.14	0.03	1.23	2.56
<i>Lacunisphaera</i>	1.21	0.86	1.05	1.04	0.18	0.22	0.63	0.91
<i>Zoogloea</i>	0.72	0.47	1.36	0.63	0.93	0.47	1.24	2.20
<i>WCHB1-32</i>	0.31	0.86	1.79	0.56	1.47	1.27	0.55	0.90
<i>Arcobacter</i>	0.35	0.18	1.19	2.92	0.34	0.29	3.51	1.56
<i>Lentimicrobium</i>	0.29	0.72	1.11	0.48	1.39	1.40	1.03	0.99
<i>Sulfuritalea</i>	0.29	3.25	0.39	1.07	0.40	1.23	1.24	0.51
<i>Thiobacillus</i>	0.25	1.14	0.92	0.79	2.40	1.70	0.65	1.03
<i>Geothrix</i>	0.01	1.94	1.17	2.40	0.23	1.42	0.47	0.64
<i>Pseudoxanthomonas</i>	1.46	1.58	0.93	1.47	2.08	1.10	0.54	0.88
<i>Geobacter</i>	0.15	7.73	2.75	2.01	1.56	2.81	0.16	0.40
<i>Dechloromonas</i>	0.68	1.02	1.11	0.94	1.17	1.27	1.34	2.14
<i>BD1-7_clade</i>	3.17	1.32	1.37	2.65	1.05	1.00	0.84	1.20

<i>Denitratisoma</i>	9.45	11.31	4.72	7.31	16.94	15.60	14.67	10.78
<i>Dokdonella</i>	9.16	3.99	8.43	8.31	7.43	7.25	9.03	7.53
<i>Arenimonas</i>	4.62	3.30	2.03	2.24	3.35	2.32	1.47	1.64
<i>Thermomonas</i>	4.30	4.61	5.08	5.32	4.90	4.48	5.48	4.83
<i>Pirellula</i>	2.61	2.42	2.71	1.74	1.47	2.16	1.12	2.65
<i>Simplicispira</i>	1.68	2.58	1.64	2.58	2.09	2.87	1.51	2.33
<i>Alicyclophilus</i>	1.67	1.99	1.82	2.98	1.96	2.14	2.51	2.55
<i>Thauera</i>	1.48	2.16	4.73	2.99	3.10	2.98	3.05	2.17
<i>Flavobacterium</i>	1.06	1.86	2.48	1.89	1.90	1.53	1.37	1.26

8.2 Submission 4 Data

8.2.1 Hydrogen Data

The moles of hydrogen were calculated using the ideal gas equation $PV = nRT$. P = pressure (1 atmosphere), V = volume (L), n = number of moles, R = gas constant (0.08206 L/atm/mol) and T = temperature (294.15 K).¹⁵⁸

Table 8-3: Volumes of hydrogen produced from each module (L)

		Module					Total
		1	2	3	4	5	
MEC	1	0.10	0.00	0.00	0.79	11.32	12.21
	2	0	0	0	0	0	0.00
	3	11.77	0.01	13.84	5.26	9.46	40.34
	4	0.39	0.02	0.10	1.74	0.00	2.25

8.2.2 P-values calculated from T table tests

Table 8-4: P-values for MECs that used recycled carbon fibre as their anode against MEC 4 (used graphite felt for the anode).

Values of 0.05 or under are considered to be statistically significant. Values over 0.05 are not significant as they have a confidence value lower than 95%.

	Anode material	P-value gas volume	P Value moles	P Value COD	P Value COD %	P Value TSS	P Value % TSS
MEC 1	M300 MnOx	0.001	0.001	0.05	0.05	1	1
MEC 2	M100 MnOx	1	1	0.1	0.05	1	0.4
MEC 3	M300 plain	0.001	0.001	0.05	0.02	0.1	0.002

8.2.3 Correlation coefficient values - Pearson

Table 8-5: Correlation coefficient values between temperature

R-Value	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode material</i>	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
<i>Current v Temp</i>	0.67	0.19	0.71	-0.01
<i>Temp v Moles H₂</i>	0.75	N/A	0.12	0.72
<i>Temp vs Gas V</i>	0.91	N/A	0.09	0.83
<i>Temp vs COD removal</i>	0.14	0.26	0.26	0.15
<i>EE vs Temp</i>	0.37	N/A	-0.12	0.61

Table 8-6: Correlation coefficient values for COD input against performance

R-Value	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode material</i>	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
<i>Current COD input</i>	-0.01	0.35	0.11	0.40
<i>Moles H₂ and COD input</i>	0.00	N/A	0.00	0.00

Table 8-7: Correlation coefficient values for the current production and recovery of hydrogen.

R-Value	MEC 1	MEC 2	MEC 3	MEC 4
<i>Anode Material</i>	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
<i>Current Moles</i>	0.82	N/A	0.62	0.07
<i>Current Gas V</i>	0.86	N/A	0.61	0.07

8.3 SEM images

Figure 8-1: SEM images of modules 1-5 of MEC 1 at 1,000 x magnification

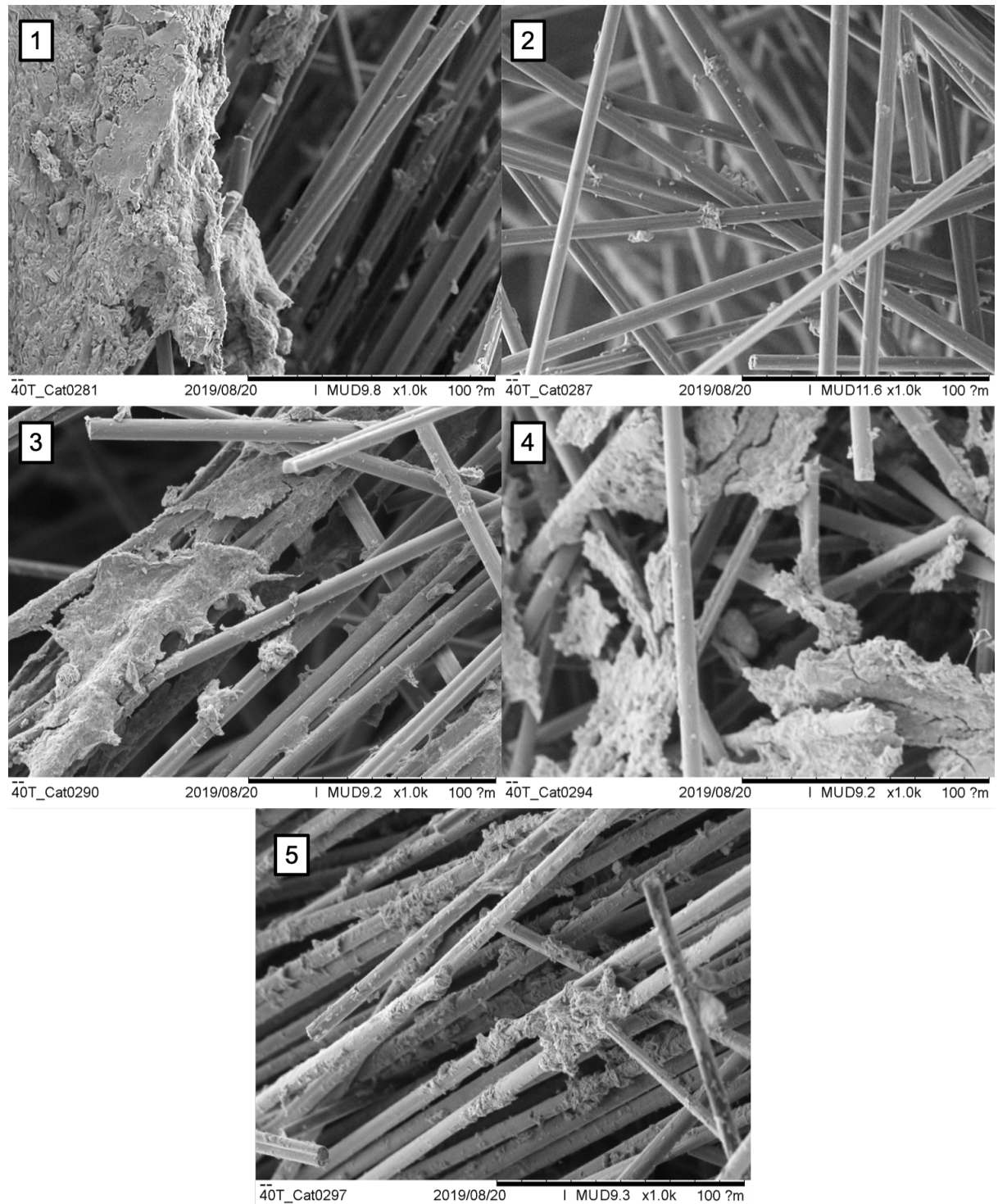


Figure 8-2: SEM images of modules 1-5 of MEC 2 at 1,000 x magnification

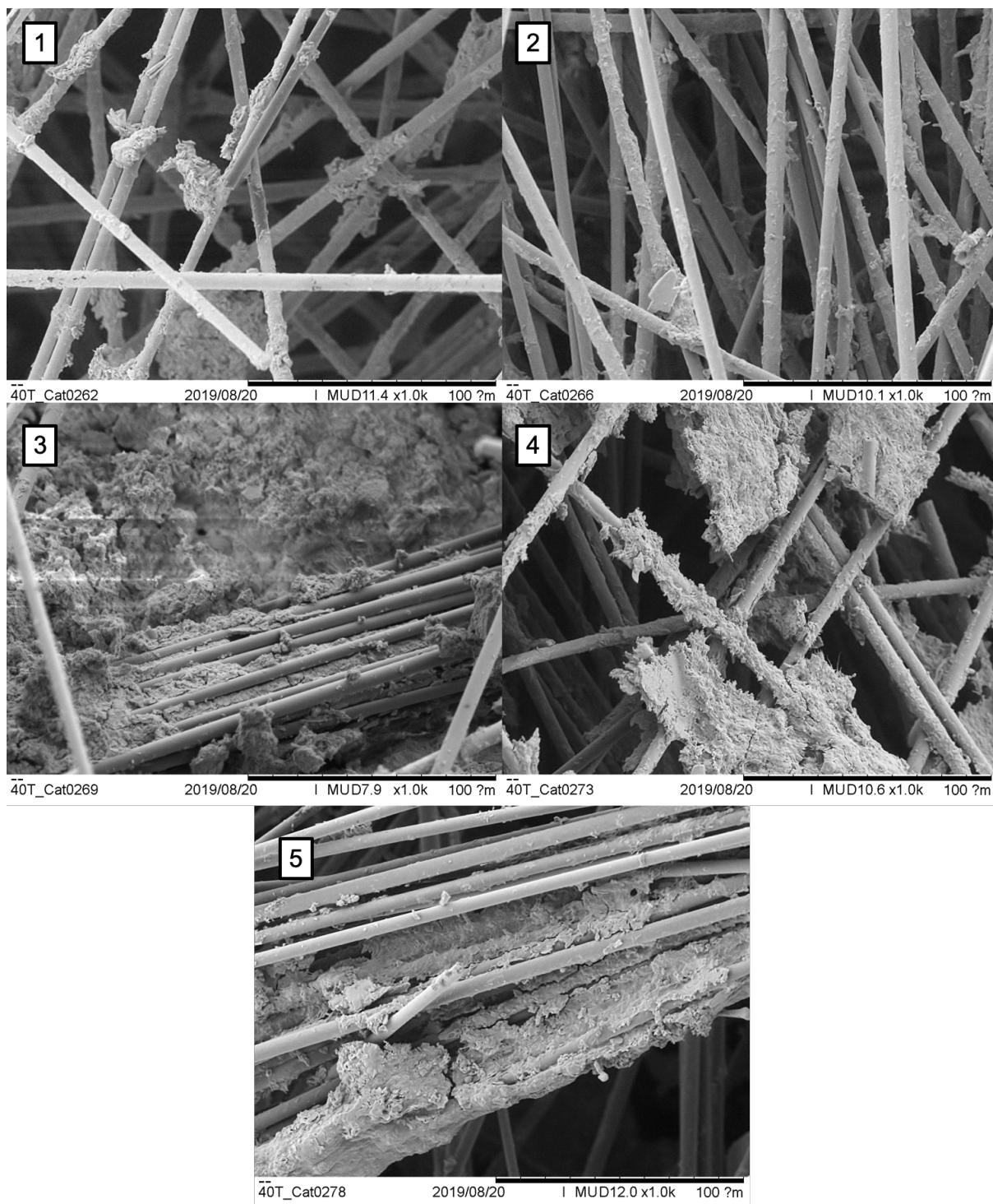


Figure 8-3: SEM images of modules 1-5 of MEC 3 at 1,000 x magnification

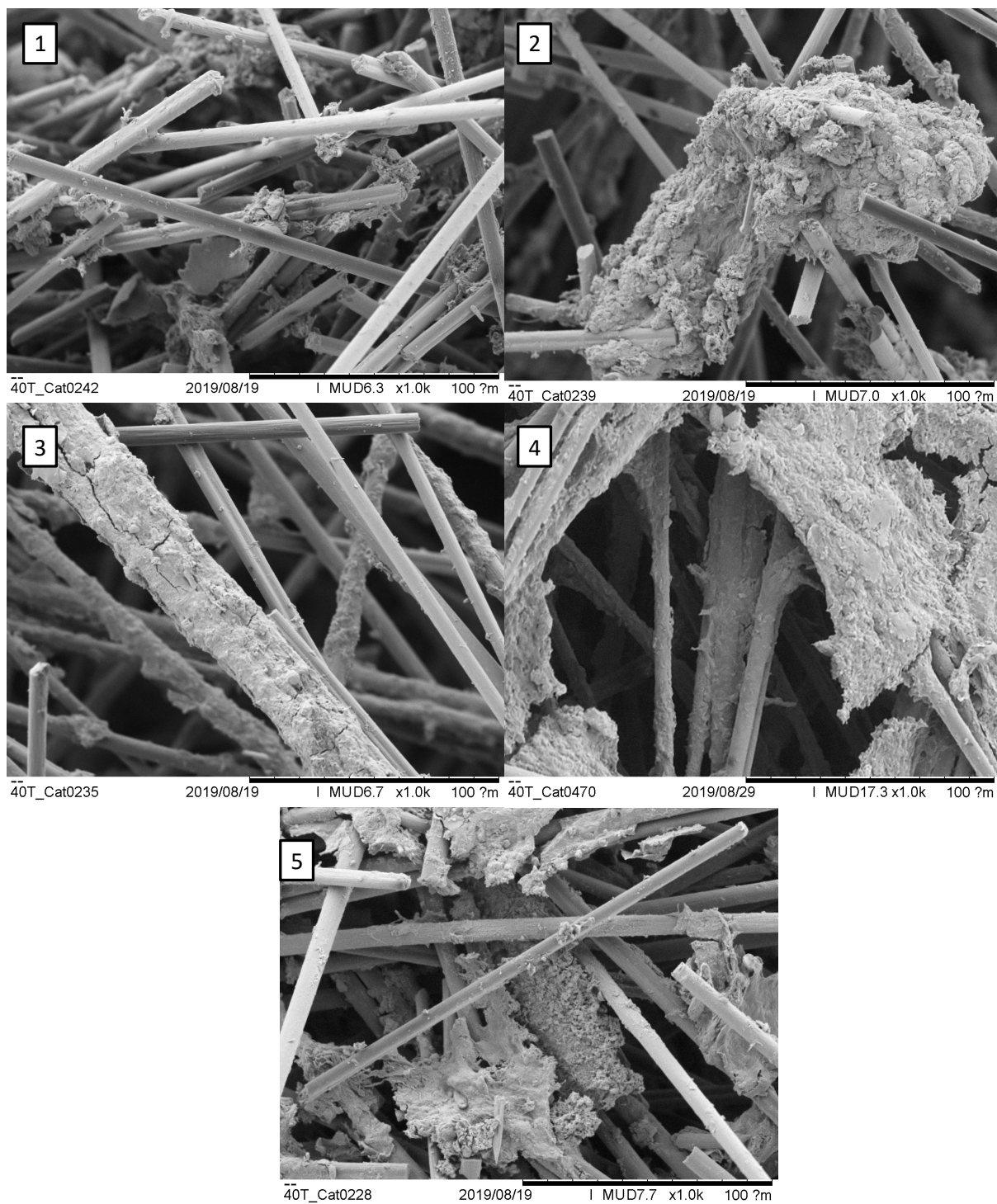
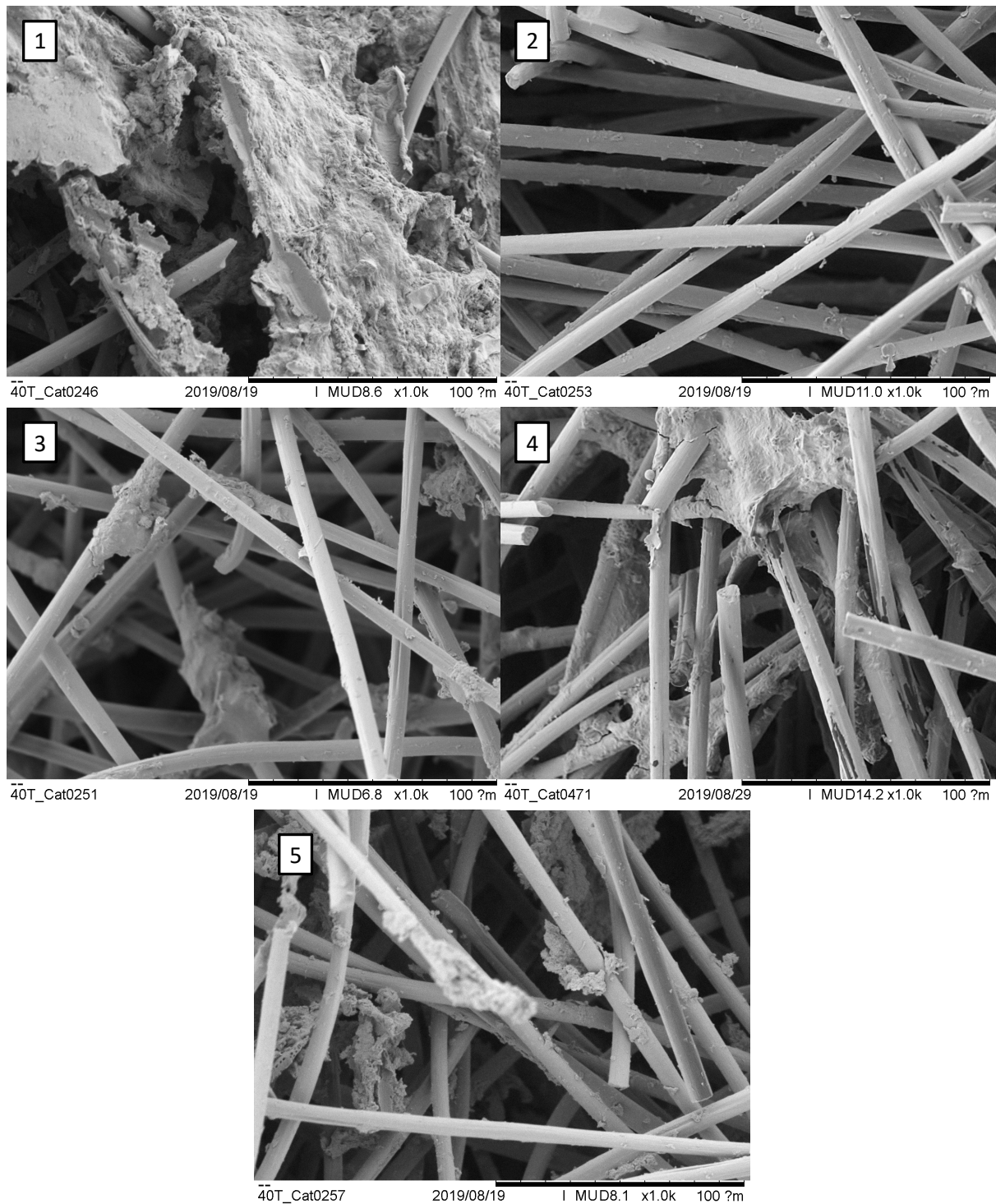


Figure 8-4: SEM images of modules 1-5 of MEC 4 at 1,000 x magnification



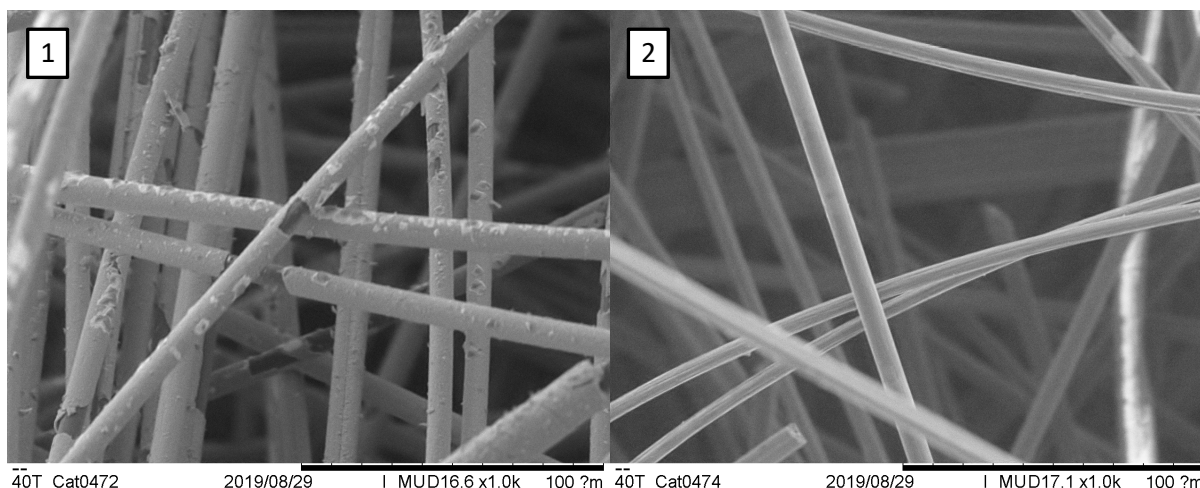


Figure 8-5: Controls of plain M300 (1) and M300 MnOx (2) anodes after SEM fixation protocol

8.4 Submission 5 Data – Cost benefit analysis

8.4.1 Manganese (IV) oxide cost calculations

Hydrogen peroxide¹⁵⁹ and hydrochloric acid¹⁶⁰ can be acquired in bulk from Easy Chemicals Trade. The costs of both chemicals for each MEC used in Chapter 4 (10 anodes) is less than £0.70 per MEC.

Manganese acetate purchase savings and use

Manganese (II) acetate can be purchased from Asia – specifically, India and imported for a significantly lower cost. An estimation of how much this would be per tonne of manganese acetate is determined in Table 8-8. The price of shipping was estimated, based on conversations with a shipping company representative, with the cost (£500) presumed to be higher than the actual cost per tonne of manganese (II) acetate.

Table 8-8: Manganese (II) acetate cost calculation when imported from India

Factor	Cost (£)
Tonne Manganese (II) Acetate Cost	1,190.00
Shipping	500.00
UK Duty at 3.5 %	41.65
Sub Total	1,731.65
VAT on sub total	346.33
Total Cost	2,077.98
Manganese (II) acetate actual cost per kilo	2.08

Using the value calculated for the cost per kilo following importation, it was possible to determine the cost for the anodes at the pilot-scale and for 1 m², which are calculated in Table 8-9.

Table 8-9: Cost of manganese (II) acetate required for electrodeposition

Scale	Mass Mn(II)Ac (Kg)	Concentration (M)	Volume (L)	Area covered (m ²)	Cost (£)
Pilot anode	0.25	0.25	4.00	0.06	0.51
Full module	0.49	0.25	8.00	0.12	1.02
Full MEC	2.45	0.25	40.00	0.61	5.10
1 m ²	4.04	0.25	65.92	1.00	8.40

The total cost saving therefore when the pre-treatment chemicals and manganese acetate costs are taken into account, the total price for the manganese coatings are £16.25 per m².

8.4.2 Calculated OpEx costs the for MECs

Table 8-10: prices of the volumes of NaCl t different scales for the upscaled 1 m³ MECs

Scale	Volume per year (m ³)	Price per year (£ year ⁻¹)
Single Cathode	0.11	0.11
Single MEC	3.58	3.55
MECs for 50,000 PE	5959.22	5920.36

Table 8-11: Running costs of the MECs in terms of electricity

Scale (m ³)	Material	Electrical energy in (kWh year ⁻¹)	Energy in cost (£)
0.08	M300 MnOx	3.92	0.44
0.08	M300 plain	7.76	0.87
1	M300 MnOx	49.00	5.49
1	M300 plain	97.00	10.86
1,666	M300 MnOx	81,630.01	9,142.56
1,666	M300 plain	161,604.18	18,099.67

The value of electrical energy is assumed as: 11.2 pence per kWh (based on the Severn Trent Water assumptions).¹⁸ Therefore the potential value of the hydrogen can be determined using the calculated moles in Table 4-11 and using the energy value for hydrogen in section 8.1.2, multiplying the number of kWh by 11.2 pence. Values are detailed in Table 8-12.

Table 8-12: Energy recovery value from hydrogen, from increased scales MECs (1 m³)

Scale (m ³)	Material	Electrical energy recovery (kWh year ⁻¹)	Energy value (£)	Price to run MEC after using H ₂ (£)
0.08	M300 MnOx	0.18	0.02	0.42
0.08	M300 plain	0.60	0.07	0.87
1.00	M300 MnOx	2.26	0.25	5.34
1.00	M300 plain	7.46	0.84	10.02
1,666.00	M300 MnOx	3,764.40	421.61	8720.95
1,666.00	M300 plain	12,433.44	1392.55	16,707.12

8.4.3 TotEx for an ASP for 50,000 PE

The CapEx for an activated sludge pool with a population equivalent of 50 thousand is approximately £3.2 million. The annual OpEx is £520 thousand. An important consideration for an activated sludge pool CapEx are the costs of the components that need routine replacement (the blowers, pumps within the system), which is referred to as the mechanical and electrical (CapEx M&E) costs. These do not last for as long as the cost of the ASP chamber (known as the CapEx Civils) and do need routine replacement every 10 years. For an ASP with a PE of 50,000 the M and E costs for 10 years are £640 thousand. Therefore, it is possible to determine the TotEx for different numbers of years (Table 8-13).

Table 8-13: TotEx for activated sludge pool

Years	TotEx (millions of £)
10	£9.04
20	£14.88
50	£32.40